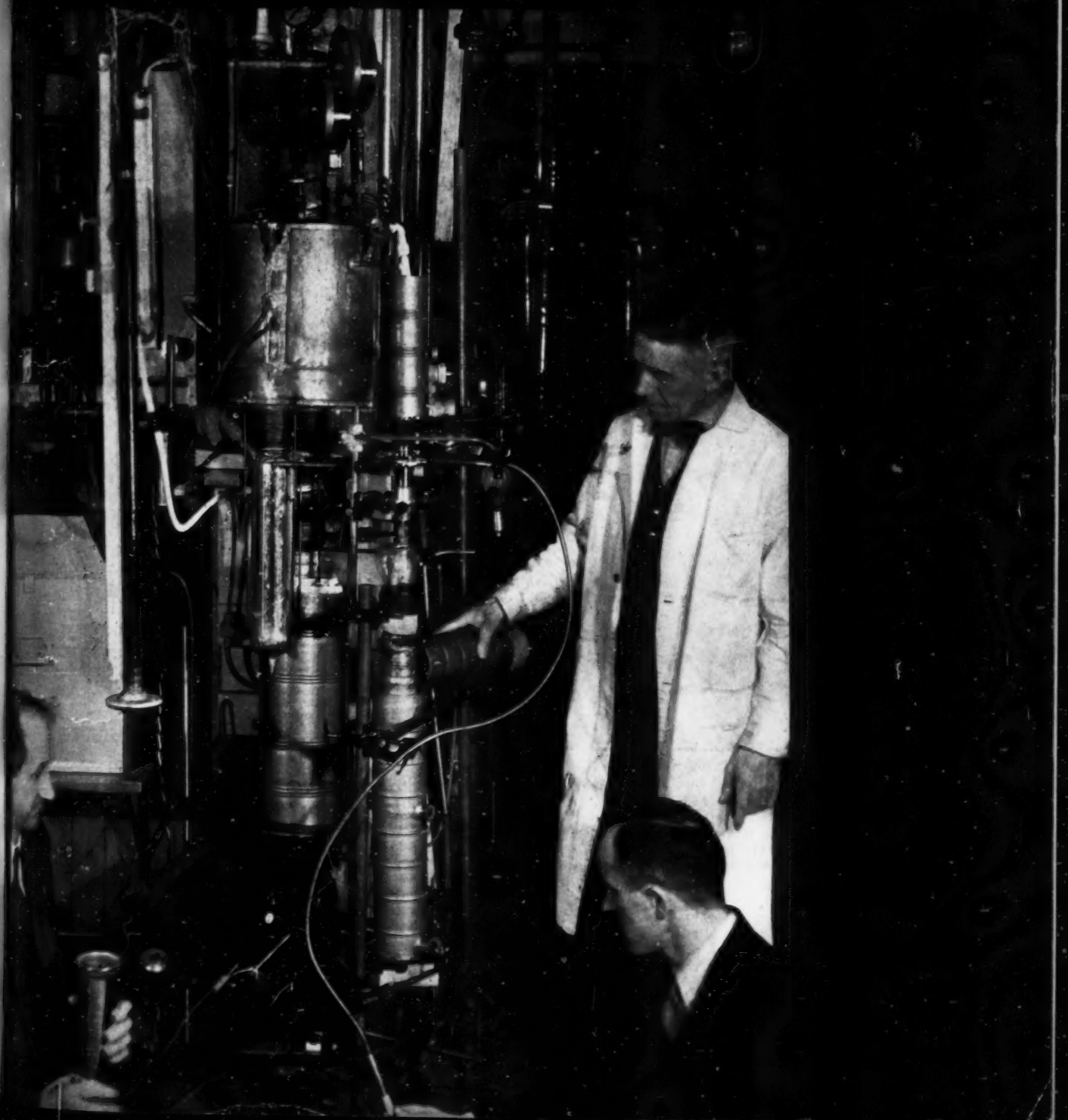
JOURNAL OF APPLIED PHYSICS



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Some Physical Phenomena at the Temperature of Liquid Helium*

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IT is taken for granted that the reader is already acquainted with what one might now almost call the classical features of low temperature investigation, such as the production of liquid hydrogen and liquid helium, the existence of superconductivity and, to a certain extent, low temperature thermometry. These phases will be dealt with in a sketchy manner and our attention will be given chiefly to the properties of liquid helium in its two states and to the magnetic peculiarities of metals in the superconducting state.

I. The Production of Liquid Helium

1. The Kamerlingh Onnes method of liquefaction.—This is merely a step by step method of producing lower and lower temperatures by the use of liquid air and liquid hydrogen. Liquid air gives a range of temperature from −182°C to −218°, or from 91°K to 55°K and liquid hydrogen from −253°C to −259°C, or from 20°K to 14°K; this may be extended to 10°K using solid hydrogen. As the boiling point of helium is 4.2°K, this leaves gaps between 55°K and 20°K and between 14°K (or 10°K) and 4.2°K. The gaps are jumped by the expansion method. As first suggested by Clusius the gap from liquid air to liquid hydrogen (from 55°K to 20°K) may be bridged by the use of liquid neon, but this would be rather expensive.

The practical difficulties in the liquefaction of helium and hydrogen are the following: (1) there must be absolute purity of the gases hydrogen and helium, (2) as both gases are hard to pump, the compressor must be very efficient, the valves being mechanically operated, and (3) there must be the very best thermal insulation.

We have been producing liquid helium regularly by this method since 1923 at Toronto; on the average one run per week throughout the academic year has been carried out, each run producing about one liter of liquid helium.

2. The Simon method.—The Simon method depends on cooling down to 15°K, in liquid hydrogen, a vessel containing helium gas at very high pressure (150 atmos.), and opening a valve so as to release the pressure. The consequent reduction of temperature is sufficient to liquefy as much as 80 or 90 percent of the helium gas. This has been used by Simon and his co-workers for rather small quantities of liquid helium, but theoretically it could be used for large quantities of liquid. The limiting feature is the ability of

* Based on lecture delivered as one of the Michael Pupin Series at the department of physics, Columbia University, New York, N. Y. February 23, 1938.

Photograph of apparatus used to measure viscosity.

the vessels to withstand pressure and still keep the heat capacity low.

3. The Kapitza method.—The Kapitza method is the result of the desire to produce a helium liquefier which would not depend on liquefying hydrogen. The precooling liquid used is liquid nitrogen; the latter is used instead of oxygen so as to have the whole operation on highly compressed gases and consequent liquids which are all chemically inert. The new feature of this method is that the gap from 60°K to 10°K in the cooling is done by means of a small expansion engine; the last step is the ordinary Joule-Thomson expansion.

4. Temperatures below 4.2°K.—Having obtained liquid helium, which has a boiling point of 4.2°K at atmospheric pressure, lower temperatures are obtained by the rapid evaporation of this liquid. It is fairly easy to obtain a temperature a little below 2°K by the use of pumps which are not of excessive capacity. At Toronto we reach by this method a limiting low point at 1.7°K. At Leiden, by the use of very large capacity mechanical pumps and consequently large capacity leading tubes, it is possible to reach 1.26°K. Using in addition a high capacity diffusion pump, Keesom has reached 0.7°K.

The lowest temperatures are produced by the auxiliary use of some salts which have paramagnetic properties at these low temperatures. When a paramagnetic substance is magnetized its temperature is raised, and conversely when it is de-magnetized its temperature falls. A mass of several grams of one of such salts is magnetized in a very strong magnetic field (10,000–30,000 gauss), while cooled to the lowest temperatures in liquid helium; the magnetizing field is then suddenly cut off, and the salt cools automatically to a still lower temperature.

Table I gives a list of salts used by various experimenters, the maximum magnetic fields employed and the estimated low temperature reached.

The actual temperature is estimated by assuming that the susceptibilities of the salts obey the Curie law, *viz.:* $\chi T = a$ constant, down to the lowest possible temperatures. When the large magnetizing field is cut off, it is not reduced right to zero, but to a field of a few hundred gauss which is used to determine the susceptibility, χ, by the method of weighing. The justification for applying the Curie law is

TABLE I.

SALTS	MAGNETIC FIELD GAUSS	LOWEST TEMP. OBTAINED	EXPERIMENTER
Gadolinium Sulphate Octahydrate Gadolinium Nitrobenzene Sulphonate Gadolinium Anthraquinone Sulphonate Gadolinium Phosphomolybdate	8000	0.25°K 0.097°K	Giauque and MacDougall
Cerium Ethyl Sulphate Cerium Fluoride Dysprosium Ethyl Sulphate	27,600	0.085°K	de Haas, Wiersma and Kramers
A Mixture of Potassium Chrome Alum and Potassium Aluminum Alum Potassium Chrome Alum	(27,600)	0.0044°K	de Haas and Wiersma
Iron Ammonium Alum Magnesium Ammonium Sulphate Gadolinium Sulphate Potassium Chrome Alum	14,100	0.038°K	Simon and Kurti

indicated by the numbers in Table II, which gives results obtained by Onnes and Oosterhuis with iron ammonium alum.

TABLE II. *Test of the Curie law for iron ammonium alum.*

$T°K$	290.0	169.6	77.3	64.6	20.4	17.9	14.7
$\chi \times 10^6$	30.4	51.8	114.7	137.0	432.0	492.0	598.0
$\chi T \times 10^5$	882	879	887	885	881	881	879

II. Low Temperature Thermometry

Under this heading we shall limit ourselves to the various kinds of thermometers which are useful in this work. In Table III is give a list of such, with their ranges and uses.

The low temperature laboratories at Leiden, at the Reichsanstalt in Berlin and at the National Bureau of Standards in Washington have given a great deal of attention to the standardization of the platinum resistance thermometer so as to establish its dependability down to 20°K.

For temperatures below 5°K, a resistance thermometer made of some alloy which tends to become superconducting at a very low temperature is the most promising. In Fig. 1 the curve ABC shows the relation between the resistance and temperature for alloys containing a constituent which is a superconductor. It is apparent at a glance that such an alloy is of no use for the regions of temperature OA and BC but would be ideal for the range AB. This involves the proper choice of an alloy and careful calibration over this range. Allen and Shire have measured the resistance of a phosphor bronze wire over a range from 1.25°K to 0.25°K, these temperatures being estimated by susceptibility measurements on a sample of iron ammonium alum.

It is doubtful if we shall ever be able to say that we have reached the absolute zero because every property of matter that we use as a temperature indicator very probably suffers a sudden abrupt change just before the absolute zero point is reached.

TABLE III. *Thermometers for low temperatures.*

KIND	MATERIAL	RANGE	USE
Gas	Hydrogen	>20°K	Measurement and Control
	Helium	> 1°K	" " "
Vapor Pressure	Oxygen	88°–55°K	Measurement and Control
	Nitrogen	77°–63°K	" " "
	Hydrogen	20°–15°K	" " "
	Helium	4°– 1°K	" " "
Electrical Resistance	Platinum	>20°K	Control
	Lead	> 7°K	"
	Alloys	20°– 0°K	Measurement and Control
Thermocouples	Various	>2°K	Measurement and Control
Magnetic	Paramagnetic Salts	1°– 0°K	Measurement

TABLE IV. *Physical properties of* He I *and* He II.

PHYSICAL CONSTANTS	BEHAVIOR AT THE λ-POINT
Density	Change in temp. coeff.
Surface Tension	Small abrupt change
Vapor Pressure	Change in temp. coeff.
Specific Heat	Discontinuous
Latent Heat of Transformation	Practically zero
Thermal Conductivity	Discontinuous
Viscosity	Discontinuous
Velocity of Sound	Change in temp. coeff.
Dielectric Constant	Change in temp. coeff.
Electrical Polarization	Continuous
Electrical Conductivity	Continuous
Molar Refractivity	Continuous

III. The two states of liquid helium

A curious change takes place in liquid helium as it is cooled down by rapid evaporation induced by rapidly pumping off the helium vapor. As indicated previously the ordinary boiling point is 4.2°K; as pumping proceeds the liquid helium visibly boils under reduced pressure, its temperature gradually falls, but suddenly when a temperature of 2.19°K is reached, the spontaneous boiling ceases, the liquid becomes quite quiescent but, as pumping continues, the temperature continues to fall, that is, evaporation continues although not accompanied by boiling. Above the temperature 2.19°K the liquid is called helium I, below that temperature, helium II, and this temperature is called the transition or λ-point. A real change takes place at this temperature, as indicated by the various physical constants of He I and He II given in the Table IV.

Of these changes in the properties of liquid helium at its transition point, many have already been described in early publications but one might profitably deal somewhat fully with the properties of viscosity, thermal conductivity, and the velocity of sound.

Viscosity measurements on the two forms were first carried out at Toronto, using the apparatus shown in Fig. 2. The method was based on the determination of the logarithmic decrement of a cylinder set rotating in the

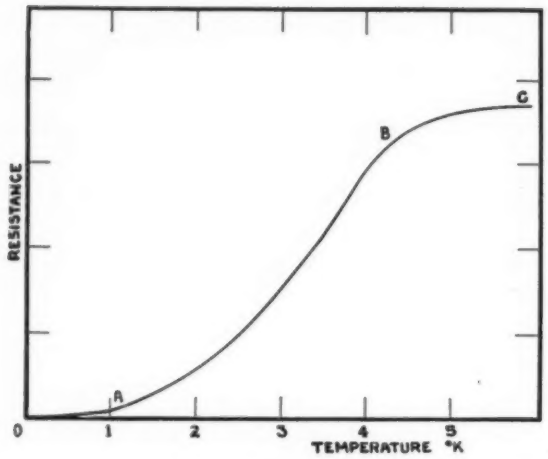

FIG. 1. Curve showing transition of alloy to the superconducting state.

liquid. These experiments showed that the viscosity of He II is only about one-tenth that of He I, in spite of the fact that the temperature of He II is lower than that of He I. The value given for He II was approximately 10^{-5} c.g.s. unit, about the value of the viscosity of air at ordinary temperature and pressure.

Kapitza (Moscow) has recently pointed out that, with the Reynolds number likely in the Toronto experiments, turbulence must have been present in the He II so that the viscosity obtained would only be an upper limit. He, and also Misener and Allen at the Mond Laboratory, observed He II apparently flowing at a measurable rate through extremely fine openings and long fine capillaries. In these experiments also, conditions of laminar flow were lacking, and in both cases an upper limit of 10^{-9} c.g.s. unit was placed on the viscosity. However, Mendelssohn at Oxford has shown that He II can creep over the surface of the glass from one container to another, and this phenomenon seems to account for the observed flow in the experiments just mentioned. Recently, at Toronto, preliminary experiments have been carried out on the flow of liquid helium through larger capillaries, and in these the previous order of magnitude of the viscosity of He II, 10^{-5} c.g.s. unit, has been confirmed, and for the slowest velocities laminar flow appeared to be attained. The flow was measured by photographing the tubes with a motion picture camera, and an enlargement of one of the pictures appears near the beginning of this paper.

Among the most startling reports regarding the change of state of liquid helium is that given out in Leiden that He II has apparently an infinite thermal conductivity, i.e., it appears to be a perfect conductor for heat. In a recent letter in *Nature*, Allen and Jones say that "Helium II is exceptional in that almost the whole of the thermal energy at the λ-point is energy of disorder. We are led, therefore, to consider heat conduction as a flow of disorder rather than as a flow of vibrational energy." This view will undoubtedly be further developed in considering the actual structure of helium II.

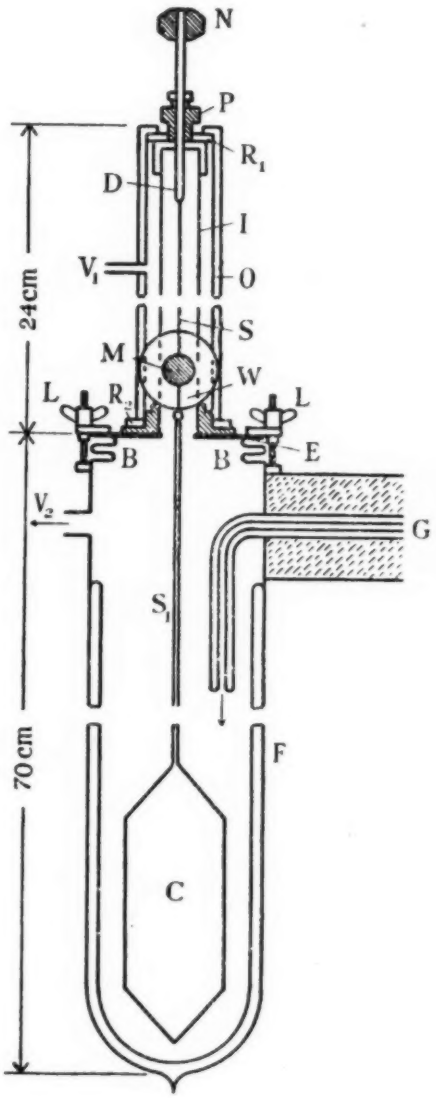

FIG. 2. Apparatus for determination of viscosity of liquid helium.

The fact that the heat conductivity is very high explains why the process of visible boiling ceases as one passes from He I to He II, although with continued rapid evaporation of He II the temperature of the liquid continues to fall.

We have just completed at Toronto the measurement of the velocity of sound in liquid helium I and II; the results are illustrated in Fig. 3.

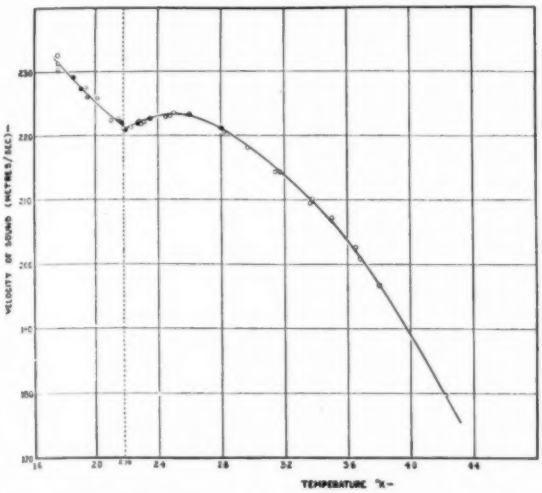

FIG. 3. Velocity of sound in helium I and helium II.

IV. The Phenomenon of Superconductivity

When Onnes first produced liquid helium he proceeded to examine the various physical properties of substances at this new low temperature. One of such properties was the resistance of pure metals. As a result of the work of Dewar and others it had already been shown that the resistance of pure metals decreased almost linearly with the temperature and promised to become zero at the absolute zero. Onnes was astonished to find that the resistance of mercury seemed to disappear completely at a temperature of 4.2°K, the boiling point of helium at atmospheric pressure. This property—now called superconductivity—has been since found to hold for 17 pure metals, as well as numerous alloys. Fig. 4 shows in a striking manner the peculiar position that these elements occupy in Mendelejeff's table.

The abruptness of the transition from a finite to zero resistance is influenced by the purity and physical form of the metal. Fig. 5 shows the curves for (1) a wire of polycrystalline tin, (2) a tin wire of several large crystals and (3) a wire

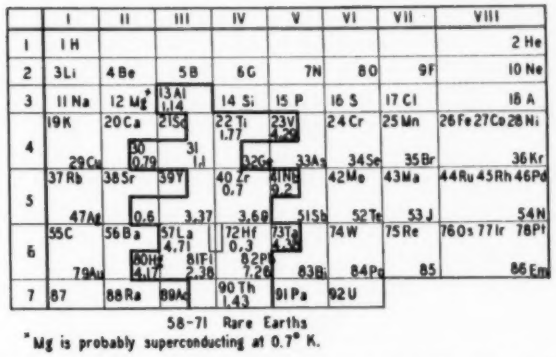

FIG. 4. Position of superconducting metals on Mendelejeff's table.

made of a single crystal of tin. Vapor pressures are indicated at the bottom of the figure and the corresponding temperatures at the top.

This property of superconductivity makes it possible to cause the curious phenomenon of perpetual currents flowing in a conducting circuit without the continuous application of an e.m.f.—the so-called persistent currents. These were first produced in lead rings, lead being a particularly useful metal since its transition point is as high as 7.2°K. The method of showing the existence of the persistent current was by means of the effect of such a current on an external magnetometer. In view of the paradoxical magnetic properties of superconductors, questions were raised as to whether the persistent current really did exist or if the effect on the external magnetometer was due to some freakish magnetic state of the superconductor.

Some of Onnes' experiments justified the theory of the existence of real currents, but

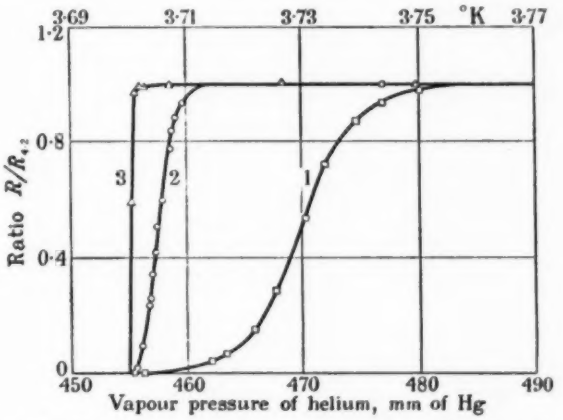

FIG. 5. Illustrating variation in transition curve of metals with physical state.

probably the most satisfactory answer to the question is given by the use of a superconducting galvanometer (at Toronto). The experimental coil, in which the persistent current existed, was connected with superconducting field coils of the galvanometer and when the persistent current was produced in the experimental coil the galvanometer gave a constant deflection.

In the early experiments the only way of getting rid of the persistent currents in a superconducting circuit was to raise the temperature of the helium bath to a point above the transition temperature of some portion of the circuit. We have devised at Toronto a very useful means of accomplishing this effect without change of temperature. About a short section of the superconducting circuit a coil of copper wire is wound; by making this copper coil of suitable dimensions, it can be arranged in such a way that a current passed through the copper coil will create a magnetic field sufficient to bring back the resistance of this portion of the superconductor and therefore suppress the persistent current in the superconducting circuit (see following section).

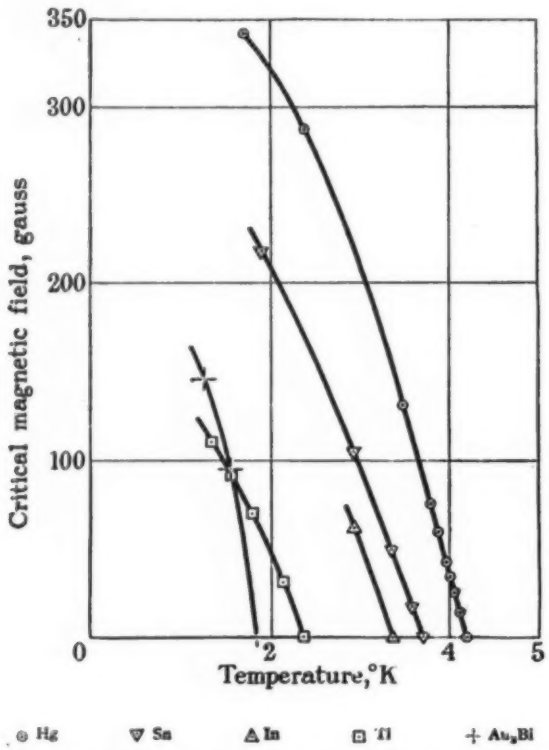

FIG. 6. Curve showing relation between threshold magnetic field and temperature for superconductors.

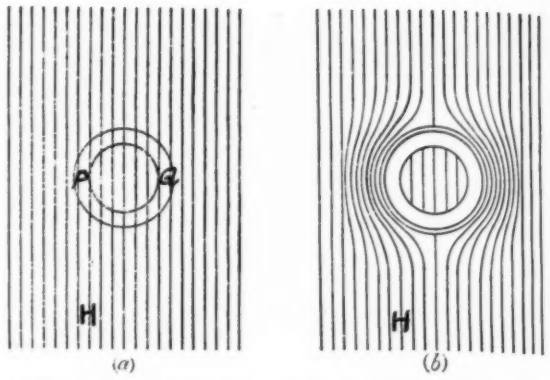

FIG. 7. Illustrating disposition of magnetic lines of force about superconductor above and below its transition point.
(a) $T>3.7°K$; (b) $T<3.7°K$.

V. The Power of External Magnetic Fields to Destroy the Superconducting State

When a metal in the superconducting state is exposed to an external magnetic field of sufficient intensity the superconductivity is destroyed or, in other words, the resistance of the metal is re-established. The greater the interval between the temperature of the specimen and the temperature of its transition point, the greater the intensity of the magnetic field required to re-establish resistance. The smallest field required to accomplish this at any temperature is called the threshold or critical field, H_c, at that temperature. Fig. 6 shows the values of threshold fields for various metals.

Since the persistent current in a conductor also produces an external magnetic field, it is possible by sufficiently increasing the current through the superconductor to bring back the resistance, the so-called Silsbee effect. At any rate, one must always take the magnetic field due to the current itself into account when dealing with the effect of an applied magnetic field.

VI. The Magnetic Properties of Metals in the Superconducting State

Meissner and Ochsenfeld were the first to draw attention to the very peculiar magnetic properties of metals in the superconducting state.

Figure 7 illustrates the essential features of this discovery; PQ represents the cross section of a hollow cylinder of superconducting metal, say, tin. In Fig. 7(a) the tin cylinder is in a uniform magnetic field, H, and at a temperature

above its transition point (3.7°K). If now, while the field is kept on, the tin has its temperature lowered to below its transition point, the lines of force assume a new distribution shown in Fig. 7(b).

It is to be noted that there is no induction inside the material of the superconductor but the field remains in the space inside the cylinder; this latter inner field remains even when the external field is removed. This remaining inner field is said to be "locked in" or "frozen in." Another way to represent the effect is to suppose that one has a cylindrical cup of a superconducting metal, say lead, in a moderately sized uniform magnetic field at a temperature above the transition point of lead. As the metal has not then any unusual magnetic properties, the lines of force may be looked upon as threading the metal and region round about uniformly. If now the temperature is lowered to below the transition point of lead, the lines of force almost entirely cease to exist in the metal itself, although they will continue to exist inside the cup and, of course, outside. Even if the outer field is removed, the inner field remains as it was originally. It might be said that one might transfer a cup of magnetic field from one place to another in the liquid helium. In other words, the superconducting metal acts as a material with almost perfect diamagnetic properties or with $\mu=0$ and $\chi=-1/4\pi$.

This curious magnetic phenomenon is of the very greatest importance in considering the theory of the superconducting state.

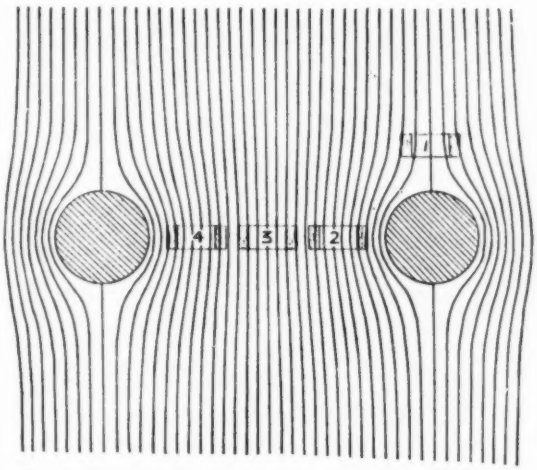

FIG. 8. Parallel cylinders of tin in a magnetic field.

A superconductor is usually defined as a body whose specific resistance is zero. For many purposes, however, it is better to avoid this term, and to consider it as a body in which an electric current, once started, flows indefinitely without the assistance of an applied field and without the generation of heat. It is therefore also a body in which an applied electric field cannot be maintained for any appreciable time. Von Laue has pointed out that if we put $\mathbf{E}=0$ in Maxwell's law of induction:

$$\text{Curl } \mathbf{E}=-\frac{1}{c}\frac{d\mathbf{B}}{dt}=-\frac{\mu}{c}\frac{d\mathbf{H}}{dt}. \tag{1}$$

Then it follows that at the surface of a superconductor the normal component of $d\mathbf{B}/dt$ must vanish, and so also the normal component of $\mathbf{B}$ itself when this was initially zero. Therefore, considered from the macroscopic point of view, a superconducting metal acts as if its magnetic permeability, μ, were equal to zero, or its diamagnetic susceptibility, χ, equal to $-1/4\pi$. This has been confirmed by many experiments.

Conversely, the view might be taken that the fundamental property of a superconductor is that its magnetic permeability is zero (up to a certain limiting value of the applied field). For consider the propagation of an electromagnetic wave in a conductor, parallel to the x axis, and defined by the electric and magnetic vectors

$$E_y=E_0e^{j\omega(t-\eta x/c)} \quad \text{and} \quad H_z=H_0e^{j\omega(t-\eta x/c)}. \tag{2}$$

The complex refractive index η is given by

$$\eta^2=\mu\left[\kappa-\frac{4\pi\sigma}{\omega}j\right], \tag{3}$$

where κ is the dielectric constant and σ the electrical conductivity; (Gaussian units are used throughout). The ratio of electric and magnetic amplitudes is further given by:

$$\frac{E_0}{H_0}=\frac{\mu}{\eta}=\left(\frac{\mu}{\kappa-(4\pi\sigma/\omega)j}\right)^{\frac{1}{2}}. \tag{4}$$

From (4) it follows that the electric field vanishes independently of the frequency when $\mu=0$. We must conclude that an electric field cannot be set up in a body whose permeability is zero, and

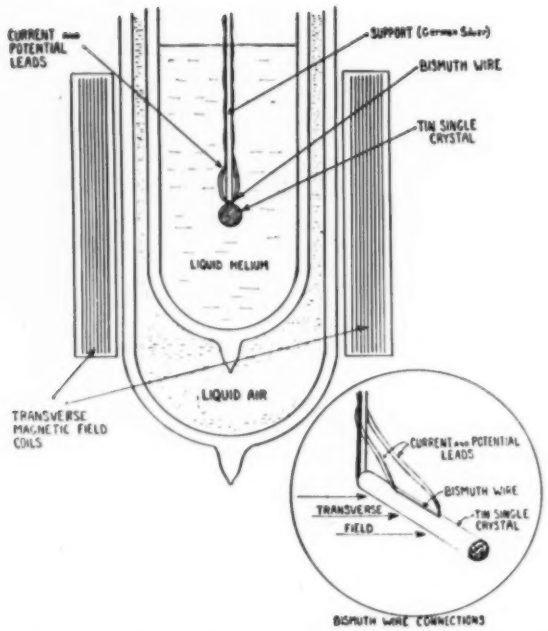

FIG. 9. Measurement of penetration of magnetic field with bismuth wire.

therefore if it is a conductor at all it must be a superconductor.

Consequently as regards bodies of macroscopic dimensions which are definitely in the superconducting state the two points of view are completely equivalent. For the discussion of a particular experiment whichever is the more convenient may be adopted.

VII. Re-establishment of Resistance and Re-acquiring of Magnetic Permeability

Later experiments than Meissner's indicate that the field is not entirely pushed out of the material of the superconducting cylinder when the latter is cooled below its transition point in a uniform magnetic field; some of the field is "frozen in" or "locked in" in the material of the cylinder.

However, if the cylinder is cooled down first to the superconducting state and then the field put on, there is no penetration of the field into the cylinder until at some point on the superconductor the magnetic intensity has reached the critical value (H_c) for that particular metal at that particular temperature.

It can be shown that the distribution of a field transverse to the superconducting cylinder (wire) is given by the following distribution (Fig. 8); this figure shows the distribution of the field about two parallel solid cylinders of a metal in the superconducting state: the cylinders are perpendicular to the direction of the field. For a field longitudinal to the cylinders there is very little distortion. In the above figure, if the applied field is equal to $\frac{1}{2}$ H_c then at positions such as 2 and 4 near the cylinders the field will be H_c and superconductivity begins to be destroyed or the magnetic field begins to penetrate the material of the superconductor.

A great deal of attention is now being given to the relation between the beginning of the return of resistance and the beginning of the penetration of the magnetic field. Such studies have led to the suggestion of the existence of an intermediate state just in the region of the transition point—a state in which the material is not completely superconducting and still not normal: probably best considered as a mixed phase in the thermodynamical sense. One line of attack is to compare, for a given temperature, the values of the external magnetic fields which (1) just begin to bring back resistance and which (2) just cause the field to begin to penetrate.

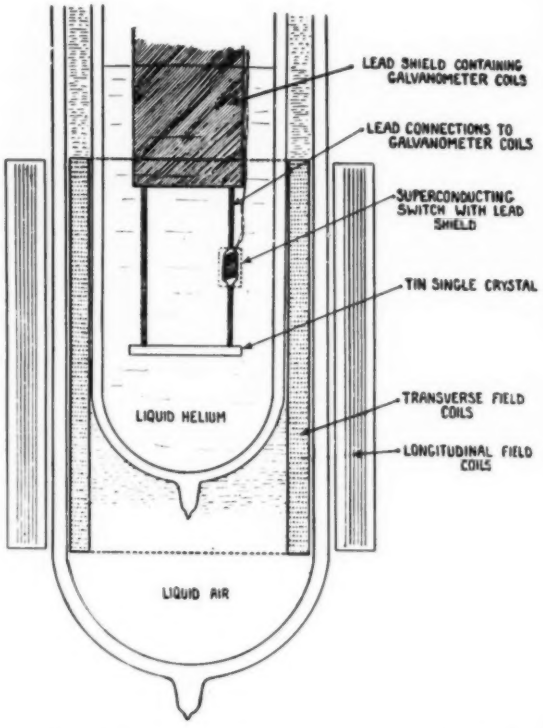

FIG. 10. Measurement of onset of resistance with superconducting galvanometer.

Two methods have been used to determine the return of resistance: (1) by actually measuring the resistance by a potentiometer method, and (2) by finding, by use of the superconducting galvanometer, the instant resistance begins to show itself by reducing and, in a short time, destroying a persistent current in a circuit.

Likewise two general methods are used to follow the change of the magnetic intensity at any point: (1) the measurement of the variation in the resistance of a bismuth wire placed where the field is to be measured and (2) by means of a current induced in a search coil, due to fluctuation of this field.

Since there is very little distortion of a longitudinal field, the value of this field which is just large enough to destroy superconductivity in a wire or cylinder is taken to be the value of H_c, corresponding to any given temperature below the transition point. The corresponding values of a transverse magnetic field are the crucial measurements. The first ones to make such measurement were de Haas and his co-workers at Leiden. They found, at the temperature of 3.22°K with a single crystal of tin, that the transverse magnetic field must have a value 0.58 H_c before resistance begins to show itself in the tin. Similar experiments have been carried out at Toronto by Mann and at Cambridge by Misener. Mann measured the beginning of penetration of the magnetic field by a bismuth wire (Fig. 9) and the onset of resistance by the superconducting galvanometer (Fig. 10) or the inductive effect in a search coil (Fig. 14). Figs. 11 and 12 show the results of these two experiments; the transverse magnetic field begins to penetrate when it reaches a value 0.50 H_c, whereas resistance does not begin to show until its value reaches 0.58 H_c (at the same temperature as de Haas used, *viz.* 3.22°K).

Calling the magnetic intensity at which the transverse field just brings back resistance, H_T, the ratios recorded above, 0.50 and 0.58, are values of the fraction H_T/H_c. Mann, using a single crystal of commercially pure tin, and Misener (Cambridge) using a polycrystalline wire of Hilger spectroscopic tin, found that H_T/H_c varied with the temperature as indicated by the accompanying curve (Fig. 13).

On the other hand Mann's most recent results with a thick cylindrical wire of Hilger spectroscope tin give $H_T/H_c=0.58$, at all temperatures.

VIII. Peculiar Time Lags Accompanying Transition from Superconducting to Normal States

In all this work on the study of what happens as the superconductor returns from the superconducting state to the normal state curious time lags have occurred which have proved very puzzling.

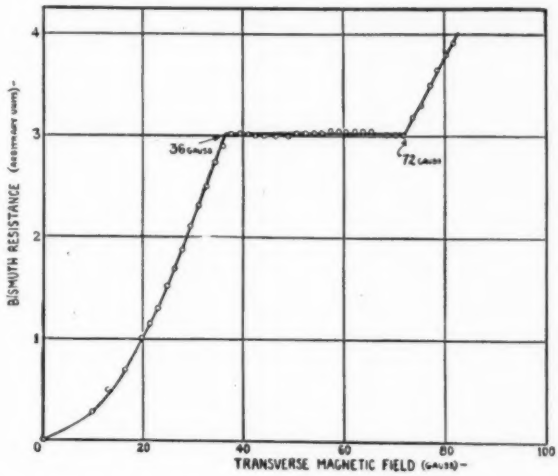

FIG. 11. Curves showing penetration of transverse magnetic field.

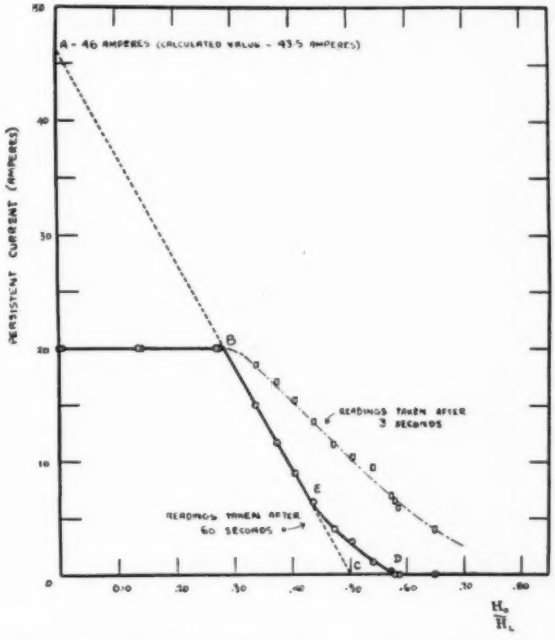

FIG. 12. Reappearance of resistance in superconductor.

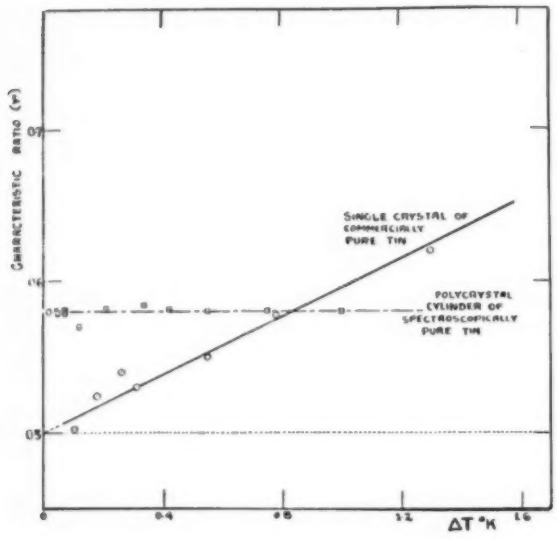
CHARACTERISTIC RATIO (r)
SINGLE CRYSTAL OF COMMERCIALLY PURE TIN
POLYCRYSTAL CYLINDER OF SPECTROSCOPICALLY PURE TIN
ΔT °K

FIG. 13. Curve showing variation in the characteristic ratio (H_T/H_c) with temperature.

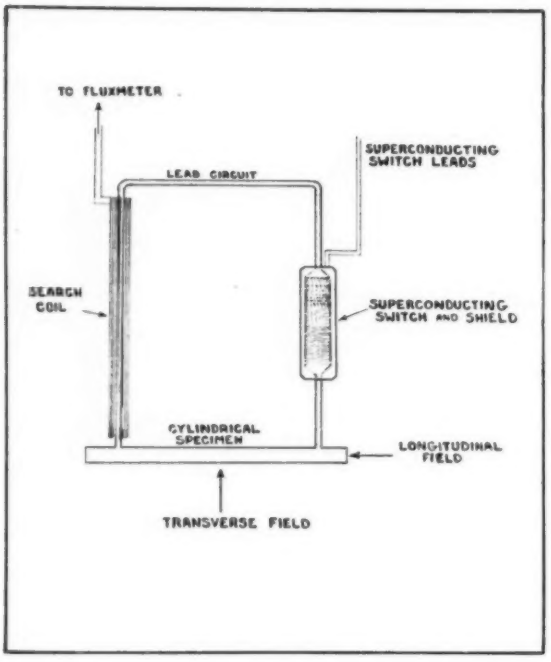

FIG. 14. Diagram of superconducting circuit for measurement of critical fields.

In carrying out the experiments for the foregoing readings, Mann found such a curious time effect in changes occurring in the persistent current in a conductor. In order to make this clear the technique of the experiment will have to be described.

This circuit is shown diagrammatically in Fig. 14. The whole of the circuit except the tin cylinder and the switch consisted of lead; as lead has a high critical magnetic field, this part of the circuit always remained superconducting for the field strengths used. The cylindrical test specimen was mounted as shown to prevent the distortions of the fields at the ends from affecting the readings. The superconducting switch was made of tin of larger diameter than the test sample, so that the magnitude of the current that the circuit could carry without resistance would be determined directly by the sample itself. To protect the switch from outside fields, a shield of lead foil was placed around it. Search coils were placed before and behind the wire in a plane perpendicular to the plane of the circuit; these coils consisted of about 200 turns of fine copper wire wound around the edges of a fiber rectangle and fastened into position so that they extended down the length of one side of the circuit. They were connected to a Grassot fluxmeter as indicated. The self-inductance of the circuit when entirely superconducting was calculated to be 85 cm.

In order to use the same field coils for both transverse and longitudinal fields, a second circuit was constructed which differed from the first in that its self-inductance was slightly higher, and the specimen was in a vertical position. Both longitudinal and transverse fields were

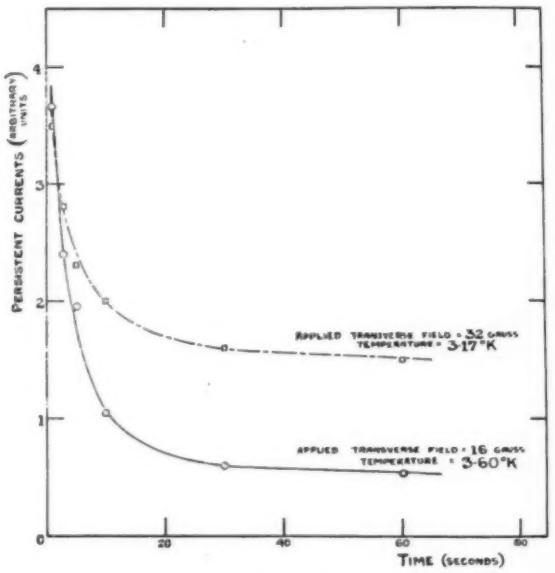
PERSISTENT CURRENTS (ARBITRARY UNITS)
APPLIED TRANSVERSE FIELD = 32 GAUSS
TEMPERATURE = 3·17 °K
APPLIED TRANSVERSE FIELD = 16 GAUSS
TEMPERATURE = 3·60 °K
TIME (SECONDS)

FIG. 15. Decay of persistent currents in tin.

supplied by a vertical solenoid, 20 cm long, which fitted around the helium flask. The solenoid was calibrated with the fluxmeter, by comparison with a standard solenoid, and it is estimated that the field measurements are accurate to within 0.5 to 1 percent.

The inducing field (not shown in the diagram) was produced by a pair of field coils outside the helium flask, and the direction of the field was perpendicular to the plane of the circuit.

An experiment consists of the following steps:

(1) Apply superconducting switch. (Circuit then nonsuperconducting.)
(2) Apply control field (transverse or longitudinal.)
(3) Apply inducing field. (No persistent current.)
(4) Remove superconducting switch. (Circuit becomes completely superconducting.)
(5) Remove inducing field. (Persistent current induced in circuit.)
(6) a. After 3 sec. apply superconducting switch and note deflection on fluxmeter.
    b. Repeat all above and apply the switch after, say, 60 seconds and read deflection on fluxmeter.

As the period elapsing between steps 5 and 6 is varied from 3 sec. up to minutes the persistent current falls from an initially higher value to a steady lower value; the temporary resistance is of the order of 10^{-12} ohm (Fig. 15). This resistance is of the right order of magnitude to make eddy currents set up in a solid sample decay in times from a few seconds to several minutes. Thus the suggestion, made by several authors, that the time effects in experiments on the magnetic properties of superconductors are due to eddy currents, is confirmed. A simple thermodynamic argument shows that eddy currents can also cause the delays in thermal equilibrium observed by Keesom and van Laer in Leiden.

IX. The Question of a Possible Lower Limit to the Linear Dimensions of a Superconducting Substance

Some years ago a considerable amount of work was done at Toronto on the superconductivity exhibited with high frequency currents and indications were given of a skin effect at the surface of the metal. As a result of this work we were led to the study of the behavior of thin films of superconducting metals deposited on a form (usually a thin wire) of nonsuperconducting

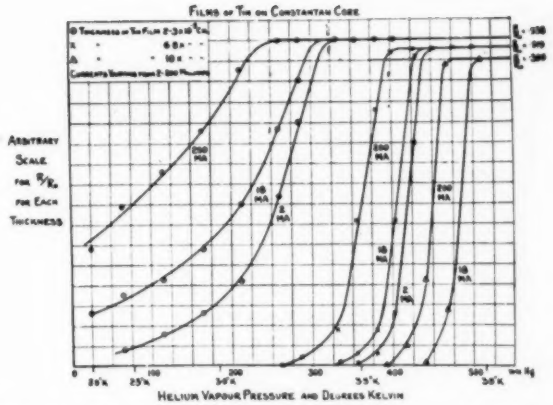

FIG. 16. Effect of current strength on films of different thickness.

metal. If the thin layer deposited on the nonsuperconducting wire became superconducting the whole conductor would act as though it were superconducting. In this way one could study the action of thin films; of course the interpretation of the results is complicated by the possibility that the superconducting metal may form an alloy on the surface with the nonsuperconducting base.

Among the results were those shown in Fig. 16.

As the thickness of the film drops to below 10^{-4} cm the transition point is lowered step by step as the thickness decreases; films of tin of thickness below 5×10^{-5} cm do not become superconducting even at 2°K (normal transition point about 3.7°K). The critical magnetic fields for the destruction of superconductivity were also very different for these thin films, but it was evident that their superconducting properties were anomalous, approaching those of alloys.

Using very fine lead wires, Pontius at Oxford has found that the critical magnetic field depends on the diameter, and von Laue has deduced from the results that the thickness of the surface layer in which the supercurrent flows is about 2×10^{-5} cm, as compared with an estimate based on classical electron theory of 3×10^{-6} cm.

The question whether there is actually a lower limit to the size necessary for the existence of superconductivity is still a very live one.

We have considered here a few of the phenomena at low temperature. While there is very little apparent indication of commercial application of the work, the field is very promising in its theoretical aspects.

Resumés of Recent Research

Recent advances in experimental and theoretical physics are described in these columns in nontechnical language. It is intended that sufficient background be given to introduce the reader to the subject.

The Origin and Requirements for Nuclear Forces

The comparison of the scattering of protons by protons with that of protons by neutrons indicates that the forces between protons and protons are nearly equal to the forces between protons and neutrons. Similarly the masses of isobaric nuclei (nuclei having the same "atomic weight") suggest that the neutron-neutron force is equal to the proton force. The current* view is, therefore, that the forces between all nuclear particles are nearly the same, except for the electrostatic force of repulsion between protons.

If the specific nuclear forces were all of the usual attractive type, the most stable state of a nucleus containing a great number of neutrons and protons would be one of great density of particles. The internal binding energy of such a nucleus would increase with the square of the number of particles and it would be favorable energetically to have very heavy nuclei. Actually neither the density nor the binding energy per particle increases with the atomic weight and sufficiently heavy nuclei are unstable. This indicates that nuclear forces are not of the ordinary type and Heisenberg, who first noticed this point, assumed that nuclear forces have an exchange character so as to prevent the increase of binding energy per particle and to secure "saturation." Heisenberg's forces are attractive for even and repulsive for odd values of the relative orbital angular momentum if the total spin of the two particles is 1. For a total spin 0 the opposite assignment of attractions and repulsions to even and odd angular momenta is made. In order to account for the high stability of the alpha-particle Majorana introduced another type of exchange force which does not depend on the relative spin orientation but is otherwise similar to Heisenberg's force. Bartlett pointed out the possibility of forces independent of relative orbital angular momentum but alternating in attractions and repulsions depending on the value of the total spin for the two interacting particles. Even though ordinary forces are unacceptable by themselves, since they do not give saturation, they may be supposed to exist to a certain extent in the presence of forces having exchange character.

Only for certain correct proportions of the above four types of forces, does one obtain saturation. Some of the corresponding conditions have been given by various authors. The paper mentioned systematizes the available information and determines the necessary and sufficient conditions making use as well of the instability of the heavier nuclei having a mass greater than 14. It appears likely, in view of the probability of certain additional simplifications, that the repulsion between protons having relative angular momentum 1 (^3P state) is between 1/3 and 3/5 of the attraction between proton and neutron in the deuteron. If it is required further that the coefficients of the four types of interaction be positive, this repulsion is restricted to the range between 11/25 and 13/25 in the same units. This repulsion is expected to show itself in experiments on the scattering of protons in hydrogen.

Similarly the likely ranges of repulsion between a proton and a neutron with relative orbital angular momentum 1 and total spin 0 (^1P) are between 9/5 and $-3/5$ on the less restricted and between 1 and 3/5 on the more restricted hypothesis.

* Breit and Wigner, Phys. Rev. **53**, 998 (1938).

New Light on the Nature and Origin of the Incoming Cosmic Rays

The big objective of many of the cosmic-ray experimenters has been to send up self-recording electroscopes practically to the top of the atmosphere, and measure the cosmic-ray ionization produced at all altitudes in a number of different latitudes. After ten years of attempts at various parts of this program by many observers, and after many blunders, too, due to inadequate techniques and insufficient knowledge, Bowen, Neher and Millikan* have recently succeeded in getting good records clear up to altitudes which are within 1.3 percent of the top of the atmosphere in four different latitudes, one at Madras, India, very near the magnetic equator, one at San Antonio, Texas (magnetic lat. 38½°N), one at Omaha (magnetic lat. 51°N), and one at Saskatoon (magnetic lat. 60°N). Also, one can now make in most cases dependable computations of the ionization clear to the top. Thanks to careful and independent theoretical computations made by LeMaitre and Vallarta and by Epstein, it now seems quite sure that no electrons of energy less than 17 billion electron volts can reach the earth vertically through the blocking effect of the earth's magnetic field at Madras. No electrons of energy less than 6.7 billion electron volts can do so at San Antonio, none of less than 2.9 billion electron volts can get through at Omaha, and none of energy less than 1.4 billion electron volts at Saskatoon. By combining this knowledge with the measured ionization produced at all altitudes in the atmosphere at each of these four latitudes it has been possible to draw the following important conclusions:

1. Practically all of the incoming cosmic-ray bullets as they come from outer space and plunge into the extreme outer parts of the earth's atmosphere consist of very absorbable rays. This means that these incoming rays must be either a mixture of electrons and photons, or else, barely possibly, of electrons alone, for these two are not easy to differentiate since both have very nearly the same absorbability. The incoming rays do not contain any appreciable number of protons or alpha-particles, or atomic nuclei of any sort.

2. The cosmic-ray effects which are found in the lower part of the atmosphere are practically all secondary effects, i.e., splashes or atomic fragments resulting from the impact of the incoming electrons and photons upon the nuclei of the atoms encountered in the very upper layers of the atmosphere.

3. Most important of all, the incoming cosmic-ray electrons have a definite banded structure in the sense that most of them have about the same energy instead of energies of widely different orders of magnitude. Specifically, the maximum of the incoming cosmic-ray energy is at 6 billion electron volts, and only a small part of it is found outside the range from three to twenty billion electron volts, thus pointing to some particular energy releasing or imparting act or acts as the cause of each cosmic ray.

4. The foregoing energy values are in just the energy range in which they should be found if the total mass-energy of the nuclei of the most abundant elements—carbon, nitrogen, oxygen, magnesium, silicon, iron—were able to be suddenly transformed into the energy of the cosmic rays, but in such a way as to conserve the momentum principle. The sudden annihilation of one atom of carbon would thus give rise to two 6 billion volt cosmic rays, the similar annihilation of an atom of oxygen to two oppositely directed 8 billion volt cosmic rays, etc.

5. It is still quite speculative to consider the foregoing as the actual mode of origin of the cosmic rays, but certainly no other mode of production of these rays has been as yet suggested that can at present marshall as good a number of agreements between theory and observation as does this one.

* Bowen, Millikan and Neher, Phys. Rev. **53**, 855 (1938).

Rigidity of Settled Pigment Layers in Paints*

BY E. L. MCMILLEN† AND D. W. GLASER‡

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SETTLING of pigment occurs to some extent in all paints and enamels, but is objectionable only when the settled pigment layer becomes so compact, granular, dry or tough that it cannot be reincorporated into the vehicle by ordinary means of stirring. Pigments which settle into a soft flocculated layer containing considerable vehicle are easily remixed into the supernatant vehicle. Objectionable hard settling may occur in flat wall paints, outside paints, floor paints, lacquers, heavy primers, and sometimes in enamels. Various agents may be added to paints to prevent or retard settling, but they often do so at the expense of the brushing or leveling qualities of the paint.

It has at times been assumed that thorough grinding of the pigment in the vehicle resulting in each particle being thoroughly wet would result in a stable suspension. This has some basis in fact for small individual particles would, of course, not settle as fast as larger aggregates or clumps of poorly ground pigment. However, all individual particles thus thoroughly wet would eventually settle to the bottom of the container if no flocculation or structure formation occurred to restrain their movement. In Table I are given the rates of fall, calculated according to Stokes' law, for individual particles of various pigments in a vehicle of unit density and unit viscosity (1 poise). Thus it becomes apparent why a well-dispersed carbon black, for example, may appear not to settle for several months or a year but after several years standing may show a firm dense deposit of the pigment at the bottom of the can. The rates of settling of the other pigments listed above are so much greater that good wetting and dispersion of the pigment in the vehicle are obviously not the means to prevent settling. Hence the only practical means available to prevent settling is by utilizing the tendency of pigment vehicle mixtures to become plastic. The strength (rigidity or yield value) of the plastic may be made sufficient to arrest the movement of the particle under the influence of gravity. It is interesting to inquire how great this rigidity must be under various circumstances. First let us consider the possibility of the vehicle being made slightly plastic itself before any pigment is added to it. (Possibly this is accomplished by the addition of such gel forming substances as aluminum stearate to the vehicle.) At any rate let us inquire what amount of rigidity in the vehicle is required to prevent the settling of a single or well dispersed individual particle of various pigments.

TABLE I. *Rate of fall of pigment particles according to Stokes' law.*

MATERIAL	PARTICLE RADIUS, CM	PARTICLE DENSITY	VELOCITY OF FALL, CM/SEC.	FALL IN 1 YEAR, CM
Whiting	2.5×10^{-3}	2.7	2.32×10^{-3}	73,100
White lead	1.5×10^{-4}	6.7	2.80×10^{-5}	883
Lithopone	1.5×10^{-5}	4.3	1.62×10^{-7}	5.11
Zinc oxide	1.25×10^{-5}	5.7	1.60×10^{-7}	5.05
Carbon black	1.00×10^{-5}	1.5	1.09×10^{-8}	0.344
Red gold sol	1.00×10^{-6}	19.0	3.92×10^{-9}	0.124

TABLE II. *Rigidity in vehicle required to support individual particles.*

MATERIAL	RADIUS CM	DENSITY GRAMS/CM³	RIGIDITY DYNES/CM²
Whiting	2.5×10^{-3}	2.7	0.73
White lead	1.5×10^{-4}	6.7	0.32
Lithopone	1.5×10^{-5}	4.3	0.021
Zinc oxide	1.25×10^{-5}	5.7	0.019
Carbon black	1.00×10^{-5}	1.5	0.0020

* This paper is part of a thesis submitted by D. W. Glaser in partial fulfillment of the requirements for the degree Master of Science in Chemical Engineering at the University of Minnesota.

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By equating the force of gravity upon the particle to the total restraining force upon the surface of a spherical particle due to the rigidity of the vehicle the least or minimum rigidities that would just support or arrest the particle were calculated (Table II). By this line of reasoning it would appear possible to absolutely prevent settling of a host of individual particles well dispersed in the vehicle if only the vehicle itself possess the absurdly small rigidity shown in Table II. That this actually may be difficult if not impossible of attainment will be discussed later.

Turning now to the other type of plasticity developed by the flocculation of the pigment vehicle mixture it is obvious that the larger clumps of particles would at first settle faster until they come to rest upon and supported each other. In this case some settling will necessarily occur, but settling will stop before a hard dry cake difficult to reincorporate into the vehicle is formed. The strength of structure required in such a case to stop the settling is given in Table III. In calculating these values it was assumed

TABLE III. *Rigidity required in bottom of container to support weight of pigment structure above. (On basis of paint containing 68 percent pigment composed of 85 percent lithopone, 15 percent asbestine.)*

CONTAINER SIZE	DEPTH CM	RIGIDITY NECESSARY DYNES/CM²
54 gal. drum	86	117,000
5 gal.	33	44,800
1 gal.	18.8	25,600
½ gal.	13.2	17,900
¼ gal.	11.3	15,400
⅛ gal.	9.4	12,800

that each layer of plastic would need to be strong enough to support the net weight of all the flocculated pigment structure above it, that the influence of the sides of the vessel could be neglected and that the greatest tendency to slip in the plastic structure would be along an angle of 45° with the direction of the compression.

In contrast to the small values of a fraction of a dyne in Table II for the case of rigidity in the vehicle, these values are enormous. The question immediately presents itself, why does not the former case behave in the same manner and compress the liquid from the lower layer. If the rigidity of the vehicle is due to some skeleton or framework of a gel forming substance such as

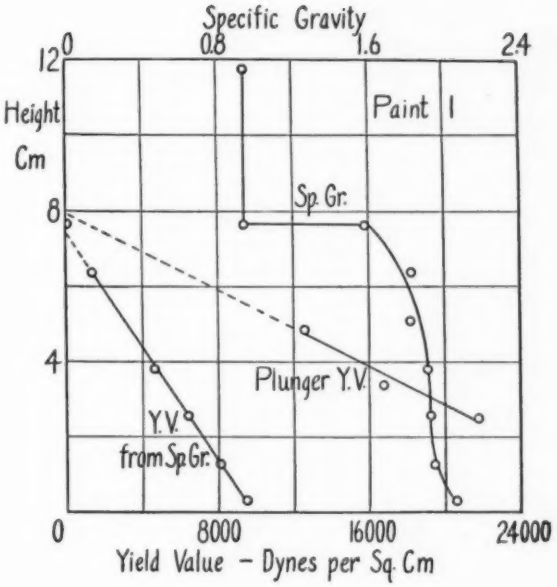

FIG. 1.

aluminum stearate this frail structure must, of course, support all the accumulated net weight of the pigment above any layer under consideration and would be subject to the same compression settling as discussed under the case where flocculated pigment is responsible for the rigidity. At best, then, slight rigidity in the vehicle can merely retard settling and make final settling possibly less severe. The rigidities in Table III are so far beyond the range of yield values found for paints at painting consistency that it is no wonder the ordinary plasticity measurements give little information about the amount of settling to be expected.

Pigment manufacturers strive to produce pigments of acceptable settling tendencies. To check on this quality the settling of paints containing the pigment in question is observed. A period of six months to a year or more is required under natural settling conditions before any conclusions may be drawn. Since this is too long a delay for proper control of pigment manufacture various accelerated settling tests[1, 2] have been devised, depending upon heat, dilution, centrifugal force and various combinations of these factors to hasten the settling. That these are not entirely satisfactory is evidenced by the fact that various procedures or cycles must be used for various types of paints. In general these tests produce

conditions not encountered in the normal shelf life of the paint and the forces involved are often more severe than that of gravity. More recently

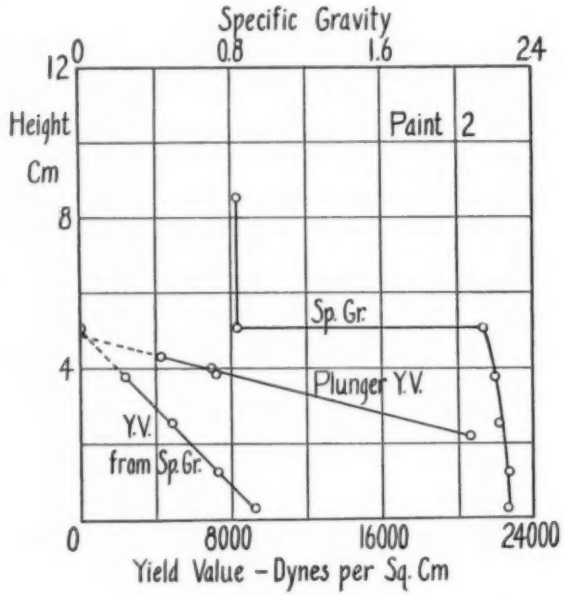

FIG. 2.

Gamble[3] concludes that the use of the torsion pendulum for studying thixotropic nature of paint does not always enable accurate prediction of the severity of settling to be expected in the paint. Thus there is a need for a rapid accurate means for evaluating the settling tendency of a given pigment in a definite paint formula.

In order to determine whether conditions in the bottoms of settled cans of paint were as postulated above, with the large value of rigidity in Table III, we examined several cans of paint which had stood undisturbed for at least 5 years, a period sufficient to approach settling equilibrium. The recording penetrometer of Werthan, Wien and Fatzinger[2] is one instrument designed to probe settled pigment layers, but it has the disadvantage that the force required to slowly force the plunger into the pigment layer is caused in part by frictional flow resistance and in part by the rigidity of the pigment layer. We desired a static measurement of the rigidity at any point in the pigment layer, and hence adopted an instrument similar to their first penetrometer.[1] For these measurements we used a small glass ball fused to a vertical glass rod and held in a rectangular yoke which surrounded the can of paint. Weights suspended from the lower part of this yoke provided the force which caused the ball to penetrate into the settled pigment layer. When any further movement of the ball ceased as observed through a cathetometer the rigidity of the pigment layer at that point was entirely supporting the force involved. From the force acting on the ball the average rigidity of the pigment layer in which the ball rested was calculated. Obviously more of the load was supported by the denser pigment layer just below the ball than by the layer adjacent to the upper part of the ball, but the values were recorded as average rigidity at the mid-point of the ball.

The specific gravities of pigment layers at different depths in these same paints were determined and from the known bulking values of the pigments it was possible to calculate the variation of percent pigment by weight with depth in the can. Also by a graphical integration it was possible to calculate the net weight of pigment above any given layer and the yield value or rigidity necessary at that point to support the pigment structure above.

Curves 1, 2 and 3 show the variation of sp. gr. with depth in the can, yield values calculated from the sp. gr. data and yield values from the

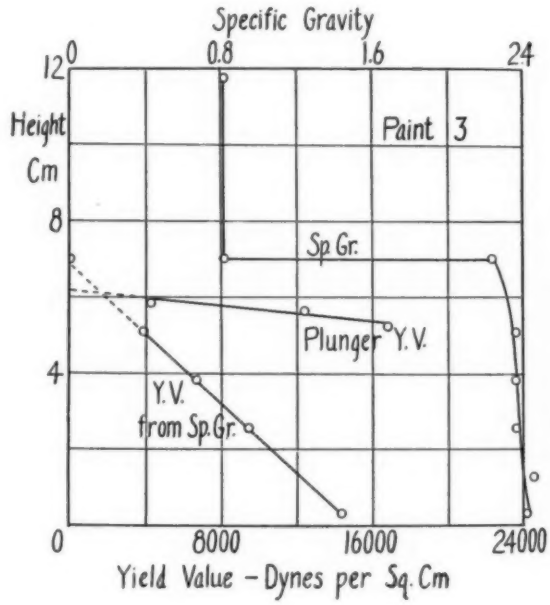

FIG. 3.

plunger tests. In general yield values calculated from the plunger data are 3 to 5 times larger than those from the sp. gr. data. This may be due in part to the bottom of the ball being at a lower depth than assumed. At any rate while the plunger data show that rigidities of tens of thousands of dynes/cm² exist in the bottoms of quart cans of settled paints, exact values cannot be obtained from it. It is easily seen that more movement in the interior of the plastic must occur than just the simple shear at the surface of the ball which was assumed in these calculations.

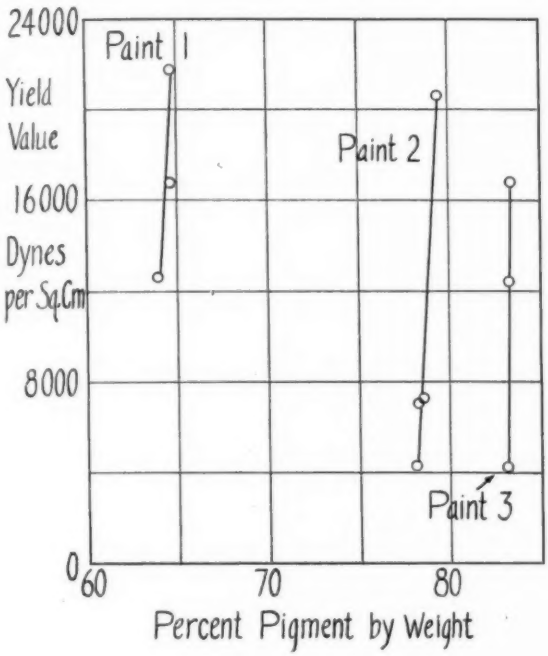

FIG. 4.

In Fig. 4 is shown the variation of plunger yield values with percentage of pigment in the settled layers. Paint 1, an outside house paint (in quart can), which possessed a 7.5 cm thick settled layer easily remixed into the vehicle, attained rigidities of 10 to 20 thousand dynes/cm² with pigment content of 63 to 65 percent by weight. Paint 2, a flat wall paint with a 5 cm layer (in pint can) which was very difficult to reincorporate into the vehicle and could be classed as a hard settled paint attained a rigidity of 10 to 20 thousand dynes in the range of 78 to 79 percent pigment by weight. Paint 3, a flat wall paint (in quart can) also was extremely hard settled and attained yield values from 10 to 20 thousand dynes when the pigment content was 83 to 84 percent. Actually such comparisons should be made upon a volume percent basis, which in this case would further emphasize the lower pigment content of the settled layer in paint 1 since it contained heavier or less bulky pigments than the other two. From this it is seen that the total weight of pigment (less the buoyant effect of the vehicle) determines the load the lowest layer of paint must support and the rigidity that must exist in that layer when settling equilibrium is attained. The paint which can attain this high amount of rigidity with the least amount of pigment will show the least objectionable settling while those requiring a high concentration of pigment in these plastic layers to attain such strengths will produce tough, dry settled layers very difficult to reincorporate into the vehicle. Thus the rate at which rigidity increases as pigment concentration is raised determines the resistance a paint will show to settling. Fig. 5 illustrates why it is that yield value measurements at painting consistency may not predict settling resistance. From measurements in the region of 50 to 60 percent pigment one might expect paint *b* to show best settling resistance. However, it is perfectly possible that in the higher concentration range found in these settled layers that paint *a* develops high rigidity at much lower concentrations than *b* and shows the less objectionable settling.

The long delay in usual settling tests is due to the necessity of waiting for the pigment concentration to increase from that of painting consistency (50–65 percent) to the higher concentration found in these settled pigment layers (60 to 85 percent) in order to determine the character of the settled layer.

It appears feasible to prepare in advance mixtures of pigment and vehicle in the range of concentration found in these settled layers and thus avoid the long period of waiting. After a short period (a few days) at rest the rigidity of these mixtures can be investigated by means of the apparatus described in this paper or by the penetrometer.

Referring to Fig. 5 it is seen that mixtures developing high rigidity at moderate pigment concentrations would tend to produce non-

objectionable settling, while those showing high rigidity only at the higher pigment concentrations would yield the objectionable type of settling.

This suggested procedure bears some resemblance to the oil absorption test in which the amount of oil to cause a given amount of pigment to ball up is measured. Certainly, other things being equal, the higher oil absorption pigments will show less tendency to settle than low oil absorption pigments. This proposed test differs from the oil absorption test, however, in that the vehicle (drying oil, thinner, drier, etc.) to be used in the paint rather than merely the drying oil is used in the test. In making the mixtures containing high pigment percentages the reverse oil absorption test procedure may have to be adopted with the pigment being added to the oil as the two are milled together. In this way it is possible to incorporate more pigment into the mixture. One possible criticism of this test for settling nature of pigments is that hard settling of pigments may be due to poorly dissolved gums, resins, or colloidal material in the vehicle tending

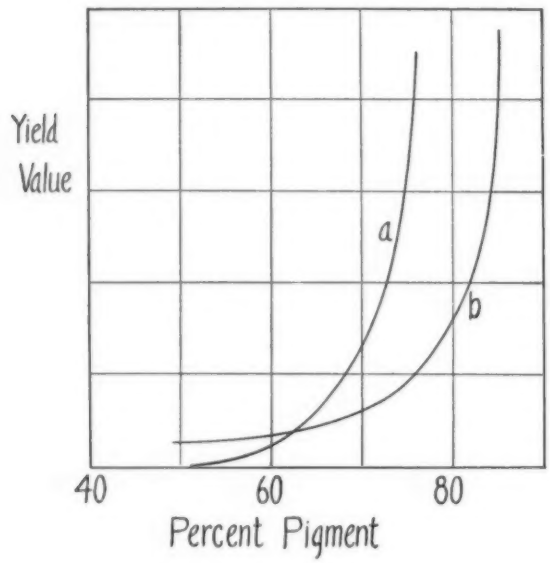

FIG. 5.

to be absorbed by and settle with the pigment to form tough settled layers as suggested by Jolly[4] and Becker.[5] In order to investigate this point we determined the percent of nonvolatile matter in hard settled layers of paint and compared them with percentage of nonvolatile in the supernatant vehicle. If any appreciable amount of resin gum or oxidized drying oil had been carried down by the pigment in settling we should expect to find a greater proportion of nonvolatile material in the vehicle contained in the settled layer as compared to that above. In a flat wall paint the vehicle obtained from hard settled layer contained 35.6 percent nonvolatile compound with 34.7 percent in the clear vehicle above. In a can of floor paint the vehicle from the hard settled layer contained 57 percent nonvolatile matter as contrasted to 54.2 percent in the supernatant vehicle. Practically no separation of gum, resins or bodied drying oil has occurred and it appears doubtful that their presence was responsible for the hard settling that occurred. Hence there is reason to believe that the test for settling outlined above will not be affected by the restriction of the amount of vehicle used. Portions of the vehicle known to be definitely absorbed by the pigments (such as water purposely added to impart a definite consistency) could, of course, be used in larger amounts corresponding to the normal paint formulation.

Summary

While various means such as finer particle size, high viscosity of vehicle and gel structure within the vehicle may greatly retard settling of pigments, it is shown that when final settling equilibrium is reached each flocculated pigment layer must possess sufficient rigidity to support the net weight of all the pigment structure above it. These rigidities are shown to vary from 10,000 dynes per sq. cm for small containers to about 100,000 dynes per sq. cm in the larger containers. Since settling will only stop when rigidities of this order are attained, the paints which attain such strength at the lowest pigment concentrations will be most easily remixed and show the least objectionable settling.

Previous settling tests upon pigments have usually utilized paint in its normal painting consistency as a starting point. Since natural or shelf settling tests require such a long time, various accelerated tests based upon dilution, heating, centrifuging and various combinations of these have been developed with the purpose of bringing about quickly the higher pigment concentrations found in settled layers. It is suggested that these

high pigment concentrations found in settled pigment layers can be brought about more quickly and directly by simply restricting the amount of vehicle in the milling of test samples of these paints. The variation of rigidity with increasing pigment content furnishes a means of predicting the severity of settling to be expected.

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If there is any period one would desire to be born in, is it not the age of Revolution; when the old and the new stand side by side, and admit of being compared; when the energies of all men are searched by fear and by hope; when the historic glories of the old can be compensated by the rich possibilities of the new era? This time, like all times, is a very good one, if we but know what to do with it.—

RALPH WALDO EMERSON
The American Scholar

Simple Electron Microscopes

BY R. P. JOHNSON

General Electric Company, Schenectady, New York

A DEVICE which images a metal surface by means of emitted electrons, rather than by reflected light, seems at first glance a most likely experimental tool. To the metallurgist it offers the possibility of studying changes in crystallization at high temperatures while these changes are occurring. To the physicist it promises immediate visual information about local variations in electron emission and about how these variations are affected by adsorbed films—information which could not otherwise be had except by tedious and indirect measurements of electron current. It is a little surprising, therefore, that in the six years since the electron microscope was christened[1] there has been no very widespread use of this tool for studying problems in metallurgy and in electron emission.

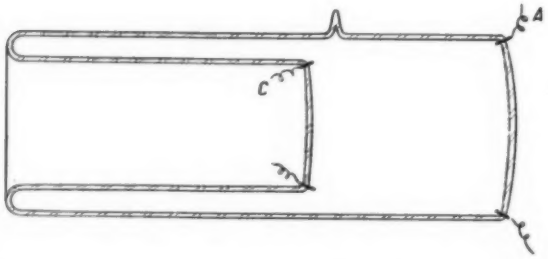

FIG. 1a. Image tube studied at the Philips Laboratory. So wide a spacing between photocathode (C) and fluorescent screen (A) is feasible only when magnetic collimation is used.*

The electron microscope itself has been developed to high excellence,[2] the optimum designs and the natural errors of electron lenses have been investigated theoretically and demonstrated in experiment, and ingenious apparatus has been contrived[3] for tracing the paths of electrons through focusing fields. But this work has been done chiefly by those who were interested in the performance of the microscope as an electron-optical device, while those who have had problems to which this new technique might profitably be applied have generally shown little eagerness to adopt it.

This reluctance presumably arises in part from a suspicion, not wholly fanciful, that an electron microscope is an essentially complicated affair, requiring for its design, construction, and successful operation no small store of skill and experience in the specialized field of electron optics. The purpose of this review is to invite attention to a class of electron tubes for which this objection does not possibly hold.

These tubes have no strict optical counterparts; they claim the name "electron microscope" only by appeal to etymology. They contain no electron lenses. They use only one high voltage. The magnitude of this voltage determines the brilliance and the definition of the electron image, but not its general fidelity. The tubes can usually be run self-rectified, with the high potential supplied by a small transformer capable of passing a few microamperes at 2000 to 5000 volts.

These tubes all operate on one simple principle: the emitted electrons are pulled across from the

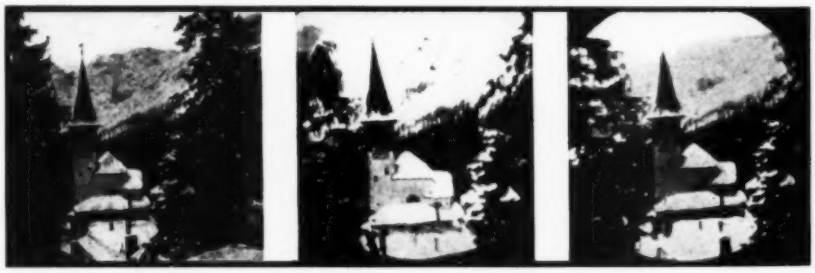

FIG. 1b. Left, direct copy from a negative; center, electron image with the tube in a long solenoid; right, electron image with the tube in a permanent ring magnet.*

* From Coeterier and Teves, Physica **3**, 968 (1936).

cathode to a fluorescent screen so rapidly that they do not have time to wander far from a straight-line path. The image on the screen is

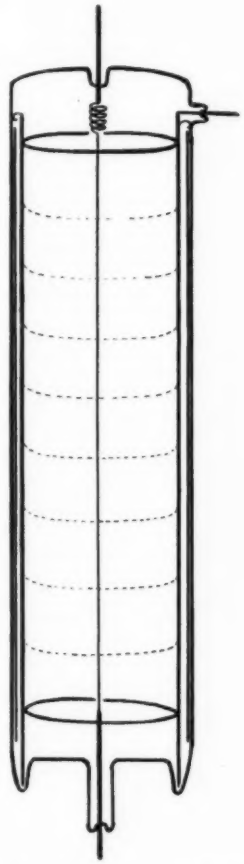

FIG. 2. A tube for imaging a cylindrical filament by emitted electrons.

simply a projection of the cathode surface, and the magnification depends on the geometry of cathode and screen. If these are parallel planes, the magnification is unity. If they are coaxial cylinders, the magnification parallel to the axis is unity, while the azimuthal magnification is given by the ratio of the two radii. If they are concentric spheres, the magnification is isotropic and equal to the ratio of the radii. If they have other figures, such as paraboloids of revolution, the magnification varies systematically from point to point in the image. All these geometrical arrangements have been employed experimentally.

The plane-parallel arrangement is typified in the image tube (Fig. 1) studied at the Philips Laboratory in Eindhoven.[4] This tube, it is true acts rather as a camera than as a microscope, but it offers a simple case for illustrating some of the features common to tubes which yield, with different geometry, a magnification greater than unity. An optical image is focused on a plane semi-transparent Cs-Cs_2O-Ag photocathode, and the photoelectrons are drawn across to reproduce the optical image on a fluorescent screen backed by a semi-transparent metal film to which the accelerating voltage is applied. The resolving power can be easily estimated. If the cathode-screen distance is d cm, if the accelerating voltage is V volts, and if small normal components of the initial velocity are neglected, an electron of mass m and charge e

FIG. 3. Electron image of a clean tungsten wire, showing die mark stripes and an underlying crystalline pattern. (The final anode in this tube was an inside wound helix, seen as diagonal black curves).

requires $d(600m/eV)^{\frac{1}{2}}$ seconds to cross the space. In this time, if the initial tangential component of velocity corresponds to an energy of ϕ volts, the electron will travel laterally a

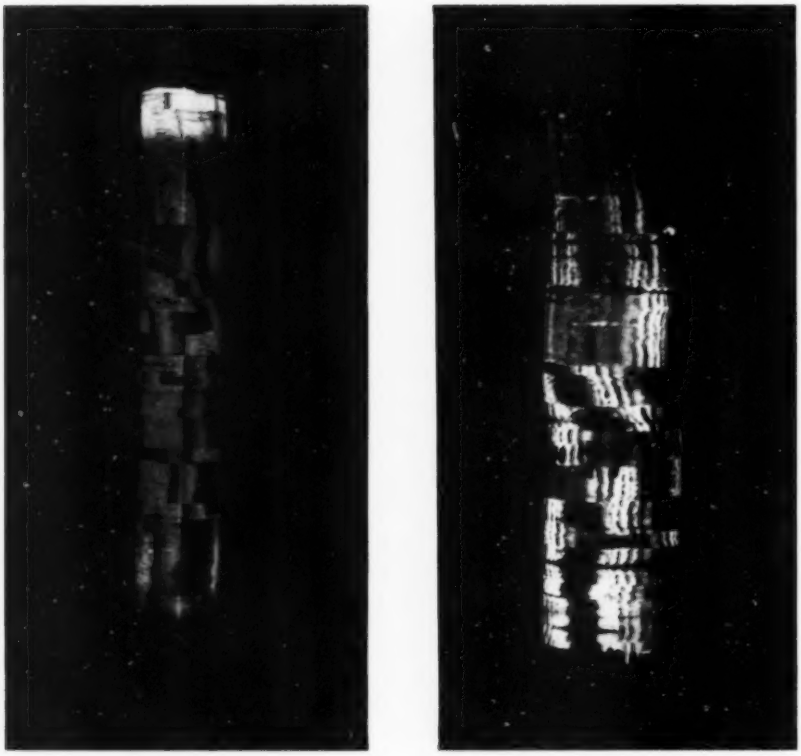

FIG. 4. Left: image of a clean tungsten wire from which the die marks have been removed by grinding. Right: image of a smooth tungsten wire on which oxygen and cesium have been adsorbed. (From experiments by R. B. Nelson.)

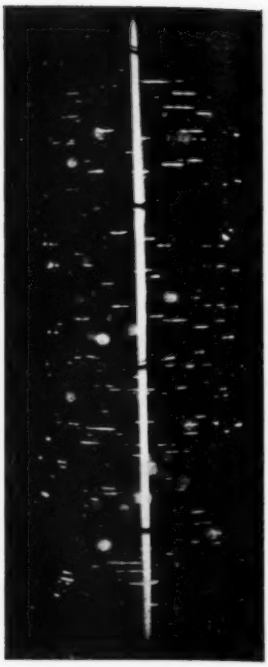

FIG. 5. Spot pattern of a thoriated tungsten wire at 1200°K, just after heating to 2800°K. The circular blurs are spots on the far side of the tube, for which the camera was out of focus.

distance $2d(\phi/V)^{\frac{1}{2}}$ cm. An emitting point on the cathode is imaged as a circular patch on the screen. Putting in some numbers: if the photoelectrons have, on the average, a tangential component of initial velocity equivalent to 2 v energy, if the screen potential is 5000 v, and if the screen is 5 cm from the cathode, the patch radius, and hence the limit of resolution, is about 1 mm. The definition is improved, for obvious reasons, by placing the tube in a magnetic field parallel with the tube axis. For reasons equally obvious, magnetic collimation is conveniently applicable only with plane-parallel electrodes.

This tube is to be compared with an image tube of more conventional design, described by Zworykin and Morton,[5] which employs a single large electrostatic lens to form an image of the emission from a large semi-transparent photocathode.

Tubes of this sort are interesting chiefly because they effect an anti-Stockes transformation of light, changing the red or infra-red image on the cathode into a green or blue fluorescent image. A passing excuse may be offered for regarding them also as electron microscopes: the fact that they reproduce fairly faithfully the shading of the optical image shows that the photocathodes are fairly uniform in sensitivity.

For the sake of introducing an idea, a slight criticism of the Philips image tube will be ventured. A metallic backing for the fluorescent screen is usually unnecessary as well as inconvenient. The common fluorescent materials emit more than one secondary electron for each primary they receive, if the energy of the primary electron lies between 300 v and 5000 v (these are very rough figures—the actual limits appear to vary widely with kind of phosphor, method of application, and the like).[6] A fluorescent screen applied directly to glass therefore floats stably only a few volts negative to any metallic final anode in the neighborhood which is held in this range of voltages. The screen receives fast electrons from the cathode and emits an equal number of slow secondary electrons to the final anode. A transverse flow of

secondary electrons, too slow to excite fluorescence and thus mar the image, also tends to keep the screen at a uniform potential. There is no reason to believe that the Philips image tube would perform much less perfectly if the phosphor were put on the bare glass and the high voltage applied to a ring of wire out in the space near the edge of the screen. In the tube of Zworykin and Morton, in most high vacuum cathode-ray oscillographs, and in most of the tubes to be described here, the screen floats, depending on secondary emission and surface leakage to keep it at a high uniform potential.

One result mentioned in the estimate of the resolving power of the plane-parallel image tube turns out to apply with equal force in any other geometry: the definition of the image decreases only with the square root of the screen voltage. The yield of light from a fluorescent screen, on the other hand, decreases at least linearly with decreasing energy of the incident electrons.[7] The image therefore grows dim faster than it grows fuzzy, and the visual impression is not greatly impaired by wide variations of screen voltage, even in the extreme case of half-wave rectified voltage. An added advantage is had, at least in theory, if the screen is detached from the final anode. When the anode potential falls below the value for which the secondary emission from the screen just fails to equal the current of primary electrons, the screen rapidly charges to cathode potential and stops the primary current. The image is thus automatically suppressed during the parts of a voltage cycle when it would be least well defined.

A cylindrical filament, heated by electric current, is the metal sample most widely used in experiments on thermionic emission and adsorption. For imaging a filament, an arrangement with cylindrical symmetry (Fig. 2) is clearly appropriate. The anisotropic magnification is a disadvantage, but for many purposes it can be tolerated. The resolving power is readily estimated. A point on the wire is imaged as a cylindrical ellipse. If the electrons are thermionic, the spread in their initial velocities corresponds to the temperature of the filament. Given a 5-mil wire at 2000°K, in a tube 2 inches in diameter, with a potential difference of 5000 v, one can distinguish points about 0.1 mm apart along the wire length, and points about 1° apart around the wire circumference.

When the cathode is an ordinary drawn wire, its image is streaked longitudinally with a system of ragged bright lines (Fig. 3), due to die mark grooves on the wire surface. These stripes, aside from their intrinsic interest, are a nuisance in that they tend to obscure more essential features of the electron image. The die marks can be removed from tungsten by abrasion,[8] by heating with a.c. in vacuum until considerable evaporation has occurred,[9] or (less successfully) by rapid electrolytic etching in NaOH or KCN.

The image of a smooth wire, if the crystals are so small that they are not resolved, is quite uniform. But if the wire contains long crystals, around each one of these the image varies symmetrically in brightness, indicating that the electron emission is different for different orientations of the underlying lattice.[10] When the wire is allowed to adsorb an activating film of alkali or alkali earth atoms (Cs, in equilibrium with the liquid near room temperature, is a convenient activator) these crystal patterns change intricately as the coverage of the wire is varied by varying its temperature. Regions that were relatively dark become relatively bright, the width

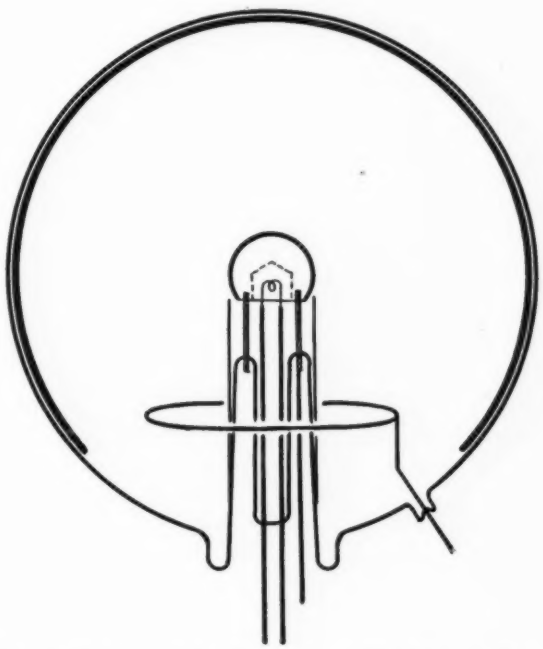

FIG. 6. Tube used by Martin and Shockley to form a spherical image of a single crystal sphere of tungsten.

of bright regions alters, and in these transitions only the symmetry of the image is preserved. When oxygen is introduced complex surface layers are formed, and symmetrical patterns of even greater variety are observed (Fig. 4). In the case of clean wires, it is not known how

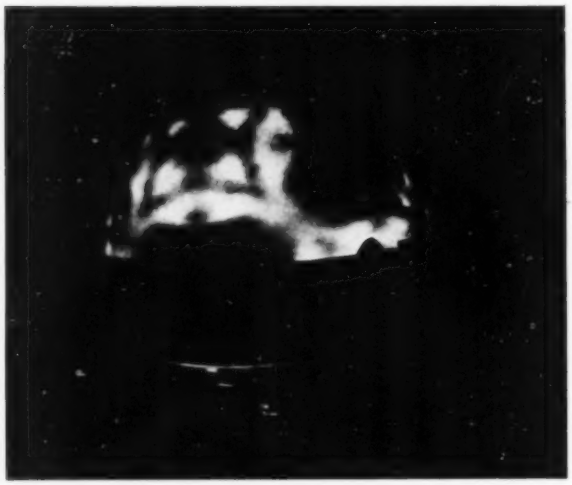

FIG. 7. Image of a single crystal tungsten sphere, in the tube of Fig. 6. The emitting surface was contaminated to an unknown degree. (From experiments by S. T. Martin.)

much of the variation of electron emission with orientation of the crystal is to be attributed to differences in surface work function, and how much to anisotropy of the electron distribution within the lattice.[11] Analogously, when the cylindrical crystals are partially covered with adsorbed films, the local variations in emissivity cannot, so far as present knowledge goes, be unambiguously assigned either to differences in equilibrium surface concentration of the adsorbed atoms or to differences in specific activating effect on surfaces of different types. The same questions arise, of course, when a flat polycrystalline sample is imaged in an electron microscope of the usual design. The crystallites are distinguishable in the image of the clean metal because, being differently oriented, they have different emission properties.[12] When the sample is activated, a complex dependence of relative brightness on average degree of activation is found among the grain images. For studying these phenomena in detail, with the aim of constructing maps of emission and adsorption properties as vector functions, the wire-in-cylinder arrangement offers certain obvious advantages, quite aside from its simplicity, over the conventional electron microscope.

The progress of recrystallization in a wire can be conveniently studied in such a tube, after the crystals have become large enough to appear as individuals in the electron image. When an activator such as Cs is used, the pattern is observable at a low temperature where crystal growth in such metals as W and Mo is negligibly slow. The cumulative effect of various heating schedules can be followed. The electron image gives immediate detailed information about crystal sizes all along the wire surface, information which would otherwise come only after tedious microscopic study. It is probably not over-optimistic to say that when emission and adsorption maps are available it will be possible to infer directly from the electron image how each large crystal in an emitting wire is oriented. Already, some inferences as to orientation can be made, solely on the basis of the symmetry of the crystal patterns. If recrystallization is to be observed while it is occurring, an activator must be chosen which remains adsorbed at the recrystallization temperature. Burgers and Ploos van Amstel[13] have used Ba and Sr to activate a polycrystalline iron strip in a conventional electron microscope, and have made motion pictures of the α–γ transition.

Wires which are activated by material issuing from the interior offer an interesting and puzzling problem. Thoriated tungsten wire, in a cylindrical fluorescent tube, shows after a high temperature flash a pattern which is spotted with tiny bright points (Fig. 5). As the temperature is raised, these points spread out into rings around the tube, and other points appear suddenly and begin to spread, until the wire is fully activated and the image correspondingly is uniformly bright. Apparently thorium reaches the surface, not by steady diffusion from within the wire, but by eruptions discontinuous in space and in time. This same behavior has been found for thoriated Mo[14] and for thoriated W in strip form;[15] in the latter case at least it appears that the eruptions do not occur preferentially at the grain boundaries. The mechanism of these eruptions is still quite obscure.

Study of field emission from cold wires is usually hampered by leakage currents, by second-

ary emission currents, and by uncertainty as to whether the emission is uniform or is localized at points which enjoy abnormal field concentration or an abnormally low work function. In the fluorescent tube these three difficulties are automatically avoided. Only the high speed electrons excite marked fluorescence, and these can be definetely assigned to their places of origin on the wire. The experiments (W, Mo, Ta, Pt, and Fe have been examined) show that a raw wire, cold, emits copiously from isolated spots when the average field is of the order of magnitude of only 10^5 v/cm. These emitting spots sometimes disappear suddenly during observation, and sometimes new spots appear suddenly. Very drastic heating is necessary, to preclude the appearance of cold emission spots at the field strengths used in observing thermionic images. Of the metals listed, Pt is the hardest to "clean." Study at higher fields, after the samples have been thoroughly outgassed, should yield interesting results.

An arrangement comprising a spherical cathode in a concentric spherical fluorescent bulb has two marked advantages over the wire-in-cylinder tube: the magnification is isotropic; if the sphere is a single crystal, the image shows, in a single observation, how the emission varies with complete variation of the lattice orientation. The spherical pattern is a complete map—with cylindrical geometry, the same map can be obtained only by composition of many images, each image showing how the emission varies in one crystallographic zone. The major experimental difficulty lies in the heating of the spherical cathode. Martin and Shockley[16] have heated a single crystal sphere of tungsten by bombardment with electrons from a filament mounted in a cavity in the sphere (Fig. 6). The electron images always show the expected crystal symmetry (Fig. 7), but their details depend with almost bewildering complexity on the nature of the surface contaminations. Another method of heating, more applicable to small spherical cathodes, has been used by Nelson. An open wound helix of thoriated tungsten surrounds the ball, and alternating high voltage is impressed between the two. On one half-cycle, electrons from the dull emitting helix heat the cathode by bombardment; on the other half-cycle, electrons from the cathode proceed through the helix to form an image on the fluorescent bulb.

High magnification is attained, with spherical geometry, by making the radius of the cathode small and the radius of the bulb large. If the spherical symmetry is distorted the image is correspondingly distorted, but a general fidelity is preserved. As the radius of curvature of the cathode is reduced, the field at the surface increases, until with a fine point it is possible, using only moderate total voltage, to draw field currents large enough to excite visible fluorescence. Müller[17] has obtained remarkable images of field emission from single crystals of tungsten and other metals, etched to points of about 1 micron radius of curvature (Fig. 8). The magnification is approximately 10^5. These patterns show that the point is emitting generally over its surface, not from isolated tiny spots. The images, like the thermionic images of more gently

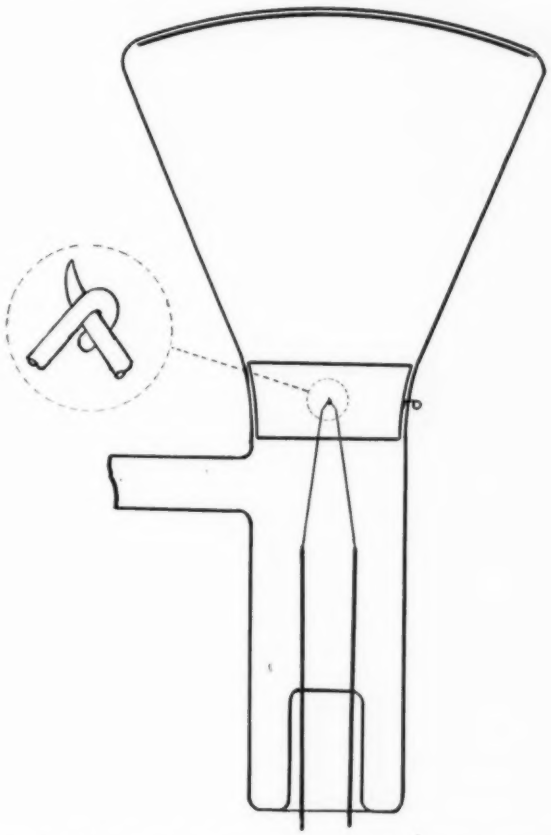

FIG. 8. Müller's tube for imaging a tiny pointed crystal by means of field electrons.*

* From Zeits. f. Physik **106**, 541 (1937).

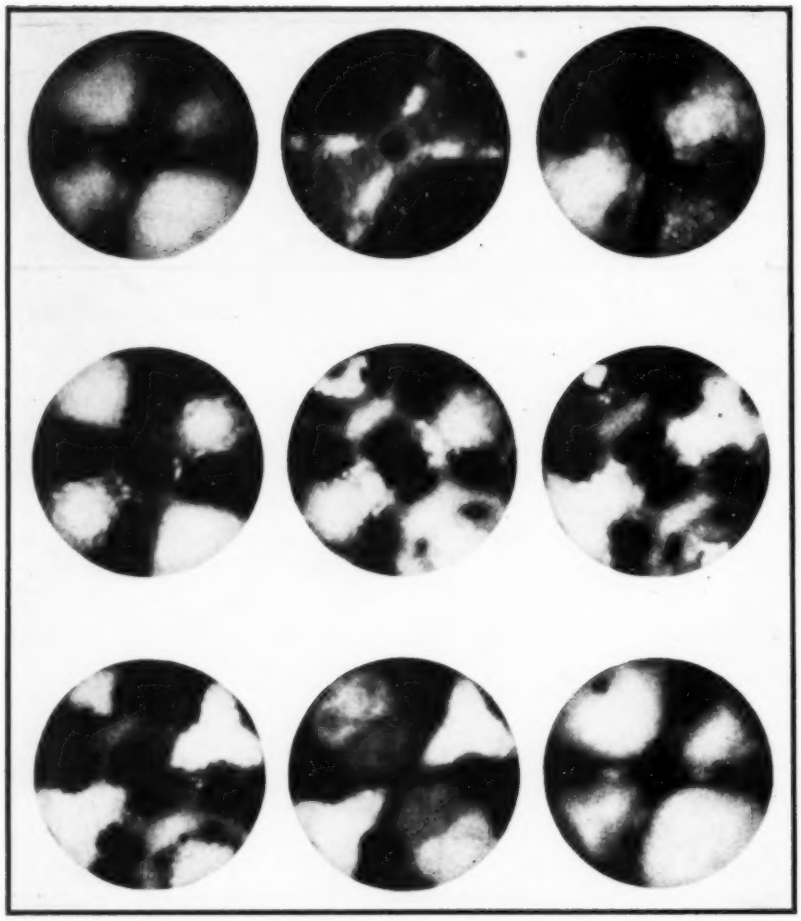

FIG. 9. Field emission patterns of a tungsten crystal, obtained by Müller with the tube of Fig. 8. The [110] axis is nearly normal to the plane of the paper, with [001] axis to the upper left. This series shows the effect of changing the oxygen coverage of the point electrode. In normal reading order: (a) After heating at 2600°K; 8100 v for 10^{-6} amp. field emission. (b) Poisoned with oxygen; 14600 v for 10^{-6} amp. (c) Heated 20 sec. in high vacuum at 1200°K; 13100 v for 10^{-6} amp. (d) Heated at 1400°K; 11600 v. (e) Heated at 1600°K; 10800 v. (f) Heated at 1700°K; 11000 v. (g) Heated at 1800°K; 11000 v. (h) Heated at 1900°K; 9500 v. (i) Heated at 2200°K; 8200 v (clean tungsten pattern).

rounded single crystals, show the symmetry of the lattice, and depend in detail on the nature of adsorbed layers (Fig. 9). Müller's experiments have been repeated and extended by Morton and Zworykin.[18]

Simple symmetry of the cathode screen arrangement is sometimes inconvenient to attain, and is fortunately not necessary. Regardless of the geometry, it is usually possible to assign each point in the image to a corresponding point on the emitter. For example, a short semicircular loop of thoriated tungsten, mounted centrally in a spherical fluorescent bulb, has recently been used[19] to demonstrate that adsorbed Th migrates toward the negative end of a wire activated by heating with d.c. (Fig. 10).

For some experiments it is necessary to have other electrodes in the space between the cathode and the screen. Such additional electrodes make no conspicuous trouble. If they are kept near the space potential, they cast an electrical shadow on the image and cause distortion only near the edges of this shadow. In this laboratory we have used two-filament cylindrical fluorescent tubes, evaporating activating material, such as Ba or Th, from one wire across to the other and studying the migration of this adsorbed material around the second wire.

Phosphors suitable for screens in these tubes are available in variety.[20] Willemite is generally very satisfactory. Uniformity of the coating is not of prime importance, since the optical transmission of the screen decreases, while the brightness of the fluorescence increases, with increasing thickness. Screens barely opaque are satisfactory. The material is conveniently applied to a curved glass surface as a thick suspension in some organic binder such as zapon, which is flowed over the surface, and after drying is baked in air to remove the binder. Alternately, the phosphor powder may be dusted onto a surface coated with potassium silicate which has been dried until it is slightly tacky, or it may be rubbed, dry, into a surface roughened by grinding or sandblasting, or it may be deposited by sedimentation from a water suspension.[21] If the tube is to contain a supply of an alkali metal for activation purposes, the screen can be protected from rapid chemical attack by coating it thinly with potassium silicate.[22]

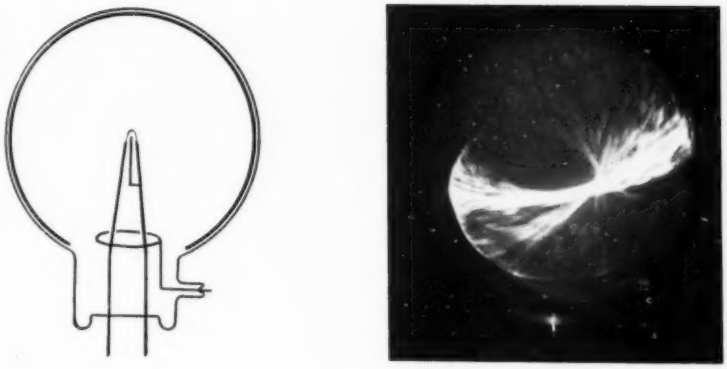

FIG. 10. Left: tube for studying the migration of Th on a short loop of thoriated tungsten wire. Right: electron image of the loop after activation by heating with direct current, with the right-hand end negative.

The ultimate brightness of the image is limited by the "sticking potential" of the screen.[6] As the voltage of the nearby metallic anode is raised, the voltage of the bombarded floating screen automatically also increases, until it reaches a value at which the yield of secondary electrons starts to fall below the primary current. The screen remains at this voltage as the anode potential is raised further, and no further increase in brightness of the pattern is effected. Except for ideally symmetric geometry, there is positive disadvantage in raising the anode above the sticking potential of the screen. The primary electrons begin to be diverted toward the anode and the image is distorted—the tube becomes a triode instead of a diode. The sticking potential is a sensitive function of the yield of secondary electrons, and hence depends critically on the condition of the phosphor surface. It is scarcely surprising that different investigators find widely different values for the same fluorescent material. In general, it appears that the sticking potential is increased if the screen is exposed to a continual slow supply of some activating material, such as is furnished in cathode-ray oscillograph tubes by evaporation from the oxide coated cathode. With willemite, in a tube containing only pure metal electrodes, it is usually safe to expect a sticking potential not lower than 3000 v.

Early in this review it was emphasized that these tubes are notable for their simplicity and for the unpretentiousness of the auxiliary equipment they require. We have recently found that, in dry weather, no formal source of high voltage is needed. The glass can be charged to a high potential by rubbing with silk, wool or paper. If the cathode is then heated, the characteristic thermionic image appears brilliantly and lasts for several seconds, long enough to be studied. This method of transient operation works successfully, of course, only with tubes in which the metallic piece conventionally used as final anode is well out of the path of the primary electrons, so placed that it exerts no marked focusing action (for example, the tube of Fig. 10 has a suitable geometry). With brisk rubbing, the glass can be charged so high that field emission from the cold cathode assembly forms a bright persistent pattern on the screen—there is obviously no question here of sticking potential. The room-temperature conductivity of the glass is high enough to let the charge leak through in a brief time, and the pattern can again be brought out by rubbing, as frequently as one wishes. Secondary emission from bombarded parts of the screen to parts not bombarded, together with surface conduction, is probably responsible for keeping the screen at a fairly uniform potential. No wandering of the pattern is observed until the screen is nearly discharged. Given low humidity, thermionic emission can be studied in tubes of this type with no auxiliary apparatus other than a battery for heating the cathode, and field emission can be studied with no auxiliary apparatus at all.

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. . . There is no such thing as an isolated fact. Every fact we discover is rooted in past knowledge and branches into the unknown. Each advance in knowledge carries the opportunity and imposes the obligation to secure more knowledge for the advancement of engineering and the good of mankind.

ARTHUR D. LITTLE in *The Chemical Engineer*, 1924

Reflections on Rupture

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I

THE rupture of solid materials is one of the most common and most unpleasant of everyday experiences. As we see them, these ruptures almost always follow the application of too great loads of one kind or another. In fact the correlation between the application of a great load and rupture is so universal and inevitable that we have acquired an intuitive feeling for the "cause" of the rupture. This we associate with the action of a force, or, if we are a little more careful, the action of a stress, in the ruptured material. This concept, of rupture caused by a stress, like many other intuitive concepts, is seldom subject to critical analysis. Experience in other fields would, however, make it not too surprising if it should prove that this intuitive and uncritical idea breaks down outside the range of experience in which it has grown up.

We almost always go further than to think that the rupture demands merely the presence somewhere of a stress or force, but, if the stress is to "cause" the rupture, we also usually demand that the direction of the force be properly related to the direction of the rupture. Thus, when we have a clean tensile break we demand that there be a force separating the particles acting perpendicular to the plane on which rupture occurs, or if the failure is by slip in shear, there must be forces tangential to the plane of shear. Otherwise we feel that there is nothing to "make" the rupture take place.

Let us look a little more carefully at what is involved in the idea of a "stress" or of a force acting on the atoms or molecules of a material. We shall, fortunately, not find it necessary to go to that degree of sophistication which considers a force as merely an aspect of the geometry of a four-dimensional relativity, but shall do our thinking with the old mechanical ideas. A force produces acceleration in the body on which it acts; if the body is stationary on the average, then the total force acting on it is zero on the average. This applies to atoms or molecules or microscopic crystalline grains no less than to the heavenly bodies to which Newton first applied his analysis. Every atom in a body which is not in the act of accelerating as a whole or in part must therefore be subject to no net force, and every atom in such a body has found such a position that it is subject on the average to no net force. The effect of applying an external force to a body, even a force up to the verge of rupture itself, is to cause the atoms to find new relative positions in which the net force acting on them will still be zero. Because the atoms move when changing their positions and because any motion which begins and stops must involve accelerations, there must be net forces on the atoms during the rearrangement which follows the application of the external force. This force, however, is evidently only an incidental epiphenomenon, because it can be made to be as small as we please by applying the load slowly enough, and can have no essential connection with the rupture which inevitably occurs when the external force passes a certain limit, independently of how slowly it may be applied. When rupture does occur, the parts of the body, and the atoms with them, receive accelerations, and there are unbalanced forces acting on the atoms. This may be stated in paradoxical fashion as follows: "A body does not break because there are unbalanced forces acting on the atoms, but there are unbalanced forces acting on the atoms because the body breaks."

The mechanism by which the atoms seek new positions when an external force is applied so as to be still subject to zero net force evidently involves a propagation of some action across the boundary of the body. When a load is applied to the body, the atoms in the surface layer on which the load acts are subject to an increased force on the side of the load which would be unbalanced

if the surface atoms did not move in such a direction as to compensate this change in the force acting from one side by a change in the force exerted from the other side by the atoms in the next layer under them. The second layer of atoms in turn now finds itself solicited by an unequal force from the two sides and moves so as to equalize this, in turn throwing the third layer of atoms out of equilibrium, which in turn moves, and so on until the change of dimensions has propagated itself throughout the entire body. The direction in which the atoms move so as to recover positions of no net force evidently depends on the direction of the external force; if the external force is a tension, then the first layer of atoms moves away from the second layer until it finds at a greater distance a greater force of attraction toward the second layer, neutralizing the greater force in the other direction of the external tension. Or if the external force is a compression, the first layer of atoms moves toward the second layer until it finds closer to the second layer an increased repulsive force sufficient to neutralize the external compression acting in the other direction.

II

The language in which we describe the "causal" relations in this situation has to be chosen with care. Thus it is safe and profitable to say that the strain in the body (that is, the greater distance of separation of the atoms) is caused by the external tension, because the strain always follows the tension, and is quantitatively connected with it, being greater the greater the tension. But it is not so easy to describe this situation felicitously in ordinary causal language from the microscopic point of view of the individual atoms, for the unbalanced forces which are the immediate occasion of their motion to new positions of equilibrium have no fixed connection with the external tension, but may be large or small at will for the same tension and the same final strain merely by applying the tension rapidly or slowly.

The interior of any body subject to the action of external forces across its free surface (we neglect the effect of "body" forces such as gravity) is the seat of stresses, and these stresses are ultimately defined in terms of the forces on the free surfaces. In general, as proved in any textbook on elasticity, the stresses are not determined solely by the external forces, but also by the elastic properties of the body. The stresses are not forces themselves, but are constructional quantities with six components, instead of the three components of a force. Given the stress, it is possible to calculate the force acting across any surface drawn in the body. The stresses are determined by the condition that the total net force on any isolated piece of the body must vanish. There is no simple connection between the stress and the net force on the individual atoms, because the latter is always zero at equilibrium, no matter what the stress. The total force acting across any plane drawn in the body is the sum of the forces exerted on all the atoms on one side of the plane by all the atoms on the other side. It is more like one-half the gross force on the atoms in distinction from the net force.

The word "stress," as used in elasticity theory, for example, has meaning only from a large scale point of view. The elements of surface across which the forces determined by the stress act must be so large in extent that the statistical effect of all the atomic forces is steady. A stress is too blunt a tool to describe small scale happenings in which the detailed play of the forces acting on the individual atoms is determinative. It is similar with the strain. The strain which enters the equations of elasticity theory is, like the stress, an average over dimensions so large as to give smooth results. Conversely, if one works from the large scale equations of elasticity theory in the elastic range, or the similarly constructed equations of plastic flow in regions of plastic deformation, one can expect to obtain no inkling of nonuniformities on the atomic scale. Consider, for example, a cylinder of plastic material which is being extended along the axis. If the extension is uniform, every cross section which was originally plane remains plane after the stretching. That is, the deformation can be described from the large scale point of view by saying that every line of particles which was originally parallel to the axis remains parallel, but extended uniformly, and every line of particles originally perpendicular to the axis remains perpendicular, but uniformly contracted. Lines of atoms thus remain lines of atoms, but their centers change in distance apart. But in the original solid material the

atoms were already practically in contact—it is not possible to crowd them much closer together, whereas the description of uniform plastic flow just given envisages the possibility of indefinitely close crowding. Hence, in the small, lines of atoms cannot remain straight after the deformation, but they must crumple, or be otherwise distorted. Any crumpling of lines of atoms may be expected to modify profoundly the properties of the substance, particularly with regard to rupture, but it is something of which no suggestion is given by the large scale description in terms of stress and strain.

"Stress" and "strain" are often used loosely, in an imperfectly defined sense, as applying when there are small scale departures from the normal regularity of atomic arrangement. This matter will be discussed again later. In this paper I use "stress" and "strain" in the precise sense of elasticity theory for large scale phenomena.

III

The idea is very common that fracture occurs when stress or strain reaches some critical value. Many attempts have been made to formulate some mathematical relation on stress or strain or both which shall serve as a universal criterion of rupture. Yet if fracture is initiated in the microscopic domain, as it seems it must, there appears to be no particular reason to expect any vital connection between such small scale happenings and stress and strain, which begin to have meaning only on a larger scale. Of course it may prove as a matter of experience, particularly in a narrow range, that the small scale happenings are determined by the larger scale stress and strain, but even so, there seems no reason to anticipate any general relation valid for all substances in all conceivable conditions of atomic disarray.

Fracture occurs in a body when the external conditions are altered if all the atoms cannot find new positions, not far from the original positions, in which they will still be subject to zero net force on the average. We have already seen that the mechanism which procures the change of position need have no simple connection with the external force which initiates the change. The mechanism procuring change of position is something automatically provided, and we need not worry too much about the details. Every atom, even at 0° Abs. is in incessant motion in a small region about its position of equilibrium, continually exploring the force field in its immediate neighborhood.

Under normal conditions, before the solid breaks, every atom is in a *stable* force field, that is, the net force called into play when the atom is displaced from its position of equilibrium is in such a direction as to restore it to its initial position. When this condition fails to hold, the atom finds itself in an unstable force field, and will presently take up a new position of equilibrium at some distance from its original position. It seems plausible to suppose that every fracture must take its microscopic beginning from some such atomic instability. Whether the instability will then spread from microscopic to macroscopic dimensions will depend in part on large scale considerations, principally on the energy. In particular, the instability will tend to spread if in this way the potential of all the forces is diminished. It seems to me that any theory of rupture must involve as an essential element a consideration of this instability factor, for certainly if there is instability there will be fracture and conversely, fracture is an instability. However, this factor is not considered by any of the present important theories,[1] some of which involve such considerations as: "At what distance of separation will the atoms exert the maximum force on each other?"

A complete theory of rupture would involve a formulation of all the conditions under which instabilities may arise. It is well known that the formulation of the conditions of stability is an extremely difficult mathematical problem. From the indifferent success of various attempts to formulate the conditions for such simple systems as regular crystal lattices it is to be expected that a general solution is at present beyond mathematical possibilities. The situation is further complicated by the probability that instabilities are almost always initiated at some imperfection in the structure, either internal or on the surface, as shown by the success of various well known recent theories of rupture. It is possible to see from certain very general considerations, however, that there are factors of instability present in any ordinary solid, even in the absence of imperfections in the structure. Under conditions of normal temperature the mean atomic forces in

solids are attractive. One can see this from the thermodynamic formula:

$$\left(\frac{\partial E}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\tau.$$

This formula states that when the dimensions of a body are uniformly reduced by the application of hydrostatic pressure, the internal energy of the body decreases at low pressures, or energy flows out of the body in the form of heat faster than it enters in the form of work done by the pressure. This means that the atomic forces do work when the distance between atomic centers decreases, which means that the forces are on the average attractive. The explanation of the fact that the solid under ordinary conditions is held distended so that the forces are attractive is to be sought in the kinetic energy of temperature agitation with which the atoms bombard each other. At very low temperatures the zero point energy may play the same role as ordinary temperature energy at higher temperatures. Imagine now the thermal energy removed from a small piece of the body and simultaneously a microscopic gap to open between two neighboring atoms. Then the strings of atoms terminating on the two sides of the gap will shorten because of the attractive forces, thus pulling away from each other and increasing the extent of the gap; in this way the potential energy of the atomic forces attains a lower value. Since the thermal energy in any part of the body is continually fluctuating, this factor making for instability is always present. From this point of view the problem becomes not to determine what it is that makes fracture occur, but how the body manages to hang together at all. Of course it must be, because bodies do hang together, that compensating fluctuations of thermal energy above the mean occur rapidly enough to annul the incipient fractures, and in fact one can see that the energy set free by the atomic forces when the incipient fracture occurs may be at once transformed into local temperature effects, just in the place needed to heal the fracture. But if the lines of atoms are too much extended, thus increasing the gain in potential energy when rupture occurs, it is to be expected that eventually large scale instability will set in. This is to be expected whether the body is extended uniformly in all three directions, or only in one or two directions. On the other hand, when the body is so much compressed that the forces are on the average repulsive, that is, when a pressure greater than $-\tau(\partial v/\partial \tau)_p/(\partial v/\partial p)_\tau$ is applied, a fracture cannot spread at the expense of the energy of the atomic forces because the widening of a fissure means a compressing nearer together of the abutting atoms and so an increase of atomic potential energy. It is not at all inconceivable, however, that the *external* forces may be so disposed that a spreading of the rupture involves a decrease of energy of the external forces more than sufficient to balance the increase of energy of the atomic forces; in this case rupture may still occur.

IV

The conditions which favor stability can be seen in a general way from the nature of the forces between atoms or atomic nuclei. If the atom as a whole is neutral, then in almost every case we have reasons, other than the thermodynamic reasons above, to believe that two such atoms attract each other when separated beyond a critical distance, and repel when nearer. If the atoms are electrically charged, then at large distances the force is mainly electrostatic, and may be either attractive or repulsive, depending on whether the net charges on the two atoms are of opposite or the same sign, but even in the case of charged atoms the force at close enough distances of approach always becomes an intense repulsion, which increases more and more rapidly as the distance of approach becomes less. In fact, the increase of repulsive force is so rapid that for many purposes the atoms can be thought of as hunks of ordinary matter, with sharp boundaries, incapable of mutual penetration. It follows that in general atomic arrangements in which the atoms are in close contact on all sides are stable, because when any atom is displaced from its position of equilibrium it must approach more closely some neighboring atom and thereby receive from it a much intensified repulsion, driving it back toward its initial position. This is why rupture is not produced by hydrostatic pressure, no matter how high (at least so long as the pressure does not break the atoms themselves) and this applies whether the substance has the regular arrangement of the crystal, or the hap-

hazard arrangement of a liquid, or is a solid with crystal structure highly disorganized by drastic deformation. If on the other hand the atomic arrangement is one with a pronounced impressed anisotropy superposed on any natural anisotropy which may be a consequence of asymmetric atomic force fields, such as is often revealed in the lattice of the crystal, then new factors making for instability may be looked for. In the following, attention will be directed principally to one particular aspect of anisotropy, namely extensions, and the corresponding instability which results in a shortening of extended fibers, but this must not be taken to imply that the shearing aspect of anisotropy, which must accompany any elongation, may not, under the proper circumstances, be followed by a corresponding instability by shearing slip. Whether instability will manifest itself by tearing or slip will depend on the structure of the body; in general slip seems to demand the cooperation of more extended domains of atoms and occurs more frequently in bodies with a large element of crystalline regularity of arrangement.

Anisotropy of distribution may be initially brought about by the action of anisotropic systems of forces on the body, either in the elastic or the plastic range. The character of the anisotropy depends not only on the external forces, but also on the atomic force fields. In particular, there is no simple connection between the direction of the external force and the resulting displacements. An example of this is the elastic lateral expansion produced in a block shortened by the action of an external axially applied compressive force within the elastic range. It is instructive to stop for a moment to analyze this situation. Let us suppose the material crystallizes in the simple cubic system. Initially, before the application of the load, the lattice automatically comes to equilibrium at such dimensions that the net force on each atom vanishes. We have already seen that this means that each layer of atoms takes up such a position that the repulsive and attractive forces of the next layer balance each other. If the lattice were completely static, symmetry would demand that the transverse spacing be uniform all the way across, up to and including the surface layer. Temperature bombardment, however, introduces an unsymmetrical element in the surface layer, so that the transverse spacing changes in the surface layer. Now apply a compressive load; the body shortens in the direction of the load, because only in this way can the outer layer of atoms on the face on which the load acts receive from the next deeper layer of atoms the repulsive support necessary to balance the action of the external force. But there is also a change of transverse spacing, and this also depends on the nature of the forces. Let us suppose in the first place that only nearest neighboring atoms exert appreciable force on each other and that this force is in the direction of the line of centers. We also neglect temperature agitation. Then we see at once that there is no transverse change of dimensions, since the distance from its transverse neighbors at which the outer layer of the lateral face finds itself in the position of no net force from its next inner neighbor is the same as before. Suppose, however, that the next nearest neighbors also act, that is, B and D act on A as well as C, still in the line of centers. If the force exerted by B and D is attractive, while that by C is repulsive, the effect of decreasing the distances from B and D to C will be to increase the component of the forces toward C exerted by B and D, with the result that A will move toward C until the more rapidly increasing repulsive force from C balances the increased component of attraction exerted by B and D. A material with forces like this would therefore contract laterally when compressed longitudinally, that is, it would have a negative Poisson's ratio. Such substances are very unusual; negative Poisson's ratios are known for certain directions in certain crystals, however, and there is nothing intrinsically im-

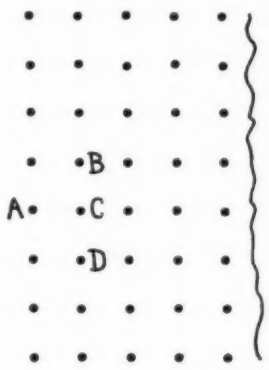

FIG. 1.

possible in such behavior, in spite of the fact that it feels wrong intuitively. It is to be remarked that no *metal* crystallizes in the simple cubic system. Suppose now that the force exerted by B and D on A is repulsive whereas that of C is attractive, as it is in the simple NaCl type of structure because of electrostatic action. Decreasing the distance from B to C and from D to C now increases the component of repulsive force urging A away from C, and the distance of transverse separation of the first and second layer of atoms will therefore increase until the increased attraction exerted by C balances the increased repulsion of B and D. Stability in the structure demands that the atoms be able to find new positions in which the attraction of C overtakes the repulsion of B and D; if no such position exists the structure becomes unstable and breaks. Substances with atomic forces such as we have just discussed have positive Poisson's ratio, as is normal.

It is important to notice that there is no component of *stress* acting in the direction of this transverse change of dimensions. Even if the distortion were pushed so far that the lateral separation is sufficient to enter the region of instability so that rupture occurs, still there would be no component of stress at the moment of rupture across the separating planes.

V

The idea of a strain component for which the corresponding stress component is zero is one which is widely accepted, and seems to cause no difficulty, but for some reason the natural extension of this to fractures with vanishing stress component is one which does cause great difficulty. The intuitive demand is very common and very strong for a stress component in the direction of fracture which shall "make" the fracture occur. It is of course evident, if the external force acting on the system is in the direction of rupture, that work is done by this force when rupture occurs, and so the mechanical principle is satisfied that systems move so as to decrease the potential energy of the forces. But the energy of the external forces is not the only energy involved—there is also the internal strain energy, and this may decrease by a pulling together of lines of atoms, as we have already seen, without the immediate accompaniment of work by the external forces. I think the intuitive demand that rupture be in the direction of the external force, or the stress, would not have arisen except for the restricted character of our ordinary experience; nearly all fractures encountered in ordinary situations, as well as those of engineering interest, are such that the direction of the fracture is the direction of the applied force. We have already remarked that both of the common manners of rupture, tensile and shearing, occur under the action of forces so applied as to increase the distance of atomic separation in the direction of fracture. But when the configuration of the external force assumes less familiar forms, one may expect the simple connection between direction of force and direction of fracture to fail, particularly if the forces are on the average compressive, so as to decrease the mean distance of separation of the atoms. When one stops to think of it, it appears that only an infinitesimal fraction of the matter in the universe is in a condition of comparative freedom or in the comparative " state of ease" of the material from which we derive our ordinary experience of fracture. All the material of the crust of the earth, for example, as well as that of all the deeper layers of the earth, is subject to enormous mean compressive stresses, and the atomic arrangement is certainly on the average removed very far indeed from that of the perfect crystal. Matter in this condition is subject to fracture, as we know from earthquakes, or from experiments on combined pressure and shearing stress.[2] Matter in the condition familiar to us occurs only in a two dimensional skin. In my work at high pressures many examples of fracture under conditions different from the ordinary have been observed, and I shall now discuss some typical cases.

The earliest and one of the most striking of such cases is the "pinching-off" effect.[3] A rod of glass or hardened steel or other brittle material passes into and out of a pressure chamber through two stuffing boxes; inside the pressure vessel it is exposed to the action of fluid pressure on the curved surface, while the ends are free. Under the action of the external pressure the rod lengthens along its axis, by exactly the same effect that produces the lateral expansion of a compressed

prism, only the effect is here doubled because the compressing force is applied along two axes instead of one. Since the ends are free there is no stress across the planes perpendicular to the axis, except inside the chamber, where there is an unimportant compressive stress because of friction as the rod elongates through the stuffing boxes. When the pressure on the outside of the rod, and accordingly the elongation along the axis, reaches a certain value, the rod suddenly breaks by a clean tensile fracture perpendicular to the axis, the two fractured pieces being expelled by the fluid pressure through the stuffing boxes. The same sort of fracturé is also produced in ductile materials, but the expelling action on the fractured fragments is complicated by the necking down which occurs before rupture, thus giving rise to a component of fluid pressure in a direction to assist the completion of the break. This component of fluid pressure results in a tension in the necked-down region, exactly like the *excess* tension in the necked-down region in an ordinary tensile test.

One of the surprising things about this phenomenon is the unanimity with which people, when they first see it, hunt for a longitudinal tensile component of stress or force, thinking that otherwise there would be nothing to "make" the rod break. For instance, one may set up the thesis that the fracture starts at surface fissures, and that at the bottom of these fissures there is a tensile stress due to the pressure exerted by the liquid on the walls of the fissure which is responsible for the fracture. Qualitatively there may be a tension of this kind, but quantitatively it is quite inadequate. Thus in the case of glass, the hydrostatic pressure necessary to produce the "pinching-off" effect is roughly equal to the ordinary tensile strength. Suppose, to be specific, that the ordinary tensile strength is 100,000 lb./in.^{2} and that the pinching-off effect is produced by a pressure of 100,000 lb./in.^{2}. In an ordinary tensile test there is an enhancement of tensile stress at the bottom of the surface fissures because of the geometrical relations at reentrant angles. Suppose, to be specific, that the maximum tensile stress at the bottom of the fissures is 125,000 lb./in.^{2}. Then the thesis is that the rod breaks in ordinary tension because the tensile stress has risen in places to 125,000 lb./in.^{2}, which is more than can be supported. Consider now the pinching-off situation. Elementary analysis shows that the complete system of stresses is the sum of two systems of stresses—the stress under simple tensile load of 100,000 lb./in.^{2} and the stress under uniform hydrostatic pressure over the *entire* external surface, including the ends, of 100,000 lb./in.^{2}. But the latter stress system is a uniform hydrostatic pressure (all three principal stress components equal) of 100,000 lb./in.^{2} throughout the interior of the body. It follows that the net tensile stress at the bottom of the surface fissures in the pinching-off experiment is 25,000 lb./in.^{2}, only one-fifth of that required by hypothesis to produce a tension failure.

Even in a structure without internal or surface imperfections, it is reasonable to anticipate that the fracture will eventually start in the microscopic domain because of some such instability as previously discussed, involving the appearance of lens shaped fissures perpendicular to the axis of the rod. Such lens shaped fissures would be unstable under a sufficiently high *transverse* load which tends to bow out the lens surfaces, increasing their curvature.

Whatever the conditions may be in the microscopic domain in which rupture starts, and whether or not fracture starts at a flaw at the surface or in the interior, there can be no question, I think, but that from the point of view of a scale large enough to give the very concept of "stress" meaning, we have in the pinching-off effect an example of a clean rupture occurring in a direction in which there is no stress component. We obviously have to distinguish between an *extension* (strain) failure, and a *tension* (stress) failure.

The stress in the pinching-off experiment can be analyzed into the sum of two stress systems: a uniform hydrostatic pressure equal to the pinching-off pressure over the entire exterior surface of the specimen, plus an ordinary tension on the ends also equal to the pinching-off pressure. The pinching-off pressure is therefore numerically equal to the tensile strength, suitably defined, which would be shown by the specimen if it were subject to a uniform confining pressure all over equal to the pinching-off pressure. This analysis holds whether or not the specimen necks down during rupture.

VI

Another striking example, which I have already discussed,[4] is that of a ring of hard rubber, fitted over a closely fitting steel core, and immersed in a fluid to which pressure is applied. When pressure rises to a few thousand atmospheres, the ring splits off the core by a clean tensile break, exactly as if it had been stretched by driving a wedge into it. This is in fact the nature of the action; the hard rubber has a rather high compressibility, so that if it were not for the restraint of the steel core it would shrink by a rather considerable amount when fluid pressure is applied. But the steel core, by preventing it from shrinking as much as it otherwise would, effectively stretches it beyond its natural figure, and this stretch may be so great that rupture occurs. However, the steel is slightly compressible, so that the rubber, even when it breaks, is still somewhat smaller than its original dimensions. Furthermore, since Young's modulus for hard rubber is comparatively small, the extra force superposed on the hydrostatic pressure necessary to stretch and break it is still much smaller than the hydrostatic pressure. We have, then, the paradox of a substance in which every strain is a shortening and every stress a compression, experiencing a clean tensile break. The break here is *against* the direction of the stress. It seems evident that it is the *distortions* in the molecular arrangements which are effective, and the fact that every distance between molecules has been shortened *absolutely* at the moment of rupture is without pertinence.

Other examples of this sort of rupture are common enough under hydrostatic pressure. Thus it is impossible to seal heavy platinum wires into glass without the seal cracking when hydrostatic pressure is applied, or a too closely fitting glass sleeve over a steel core will crack at high pressure, exactly like the hard rubber ring. It is easy to mention unequal compressibility, and to think that the explanation is the same as that for the familiar cracking that occurs when a seal of an unequally expansible metal and glass is cooled. But in this latter case net tensile stresses are produced on cooling, whereas in the case of breaking under hydrostatic pressure, the superposed tension which is necessary to stretch the glass over the metal is less than the hydrostatic pressure, so that the total resultant stress is compressive in every direction. Again it is evident that the character of the stress is not the determining factor, but the geometrical distortion must be a very important if not the unique factor.

The relations are so paradoxical here that it may pay to dwell a little longer on the matter by means of an idealized experiment, not very far removed from what has actually been done in the laboratory. Imagine, then, a bar of hard rubber of 1 sq. in. section which can be loaded longitudinally by a load hung on it, enclosed, with the load, in a chamber filled with a fluid on which hydrostatic pressure can be exerted. We suppose the normal breaking strength is 5000 lb./in.^{2}. The rod would then break under a load of 5000 lb. when the pressure in the fluid is zero. Now apply pressure to the fluid, up to 100,000 lb./in.^{2}, to be precise. Then we may suppose, to be general, that there has been some change in the tensile strength of the rubber, but, in any event, we suppose that the increase in tensile strength is not as great as the applied pressure, that is, the strength is now less than 100,000 lb./in.^{2}. If justification for this is felt necessary, it can be found in various experiments, in particular, the recent ones of Griggs on limestone;[5] he found an increase in tensile strength under pressure, but by an amount very much less than the increase of pressure itself. Suppose now that the strength of our hard rubber rod is 10,000 lb./in.^{2} under 100,000 lb./in.^{2} pressure. This means that the rod breaks when a weight of 10,000 lb. is hung on it, when immersed in the fluid under 100,000 lb./in.^{2}. The rod thus breaks *against* a net compressive stress of 90,000 lb./in.^{2}. In spite of this, the mechanical principle that the potential energy must diminish is not violated, because the work done by the fluid rushing into the fracture at 100,000 lb./in.^{2} more than compensates the work done against the force of 90,000 lb./in.^{2} on the end where the weight is applied. Superposed on this there is an additional work done by the fluid, because at the moment of rupture there is a net decrease of volume of the entire rod.

Both of these examples, that of the pinching-off effect and of the cored ring, are understandable from the point of view of atomic instability

as the determining factor in initiating rupture In our discussion of both these examples we found it suggestive to resolve the actual stress system into the sum of two systems, a hydrostatic pressure and a superposed tension, and we saw that qualitatively the fracture occurred as if the tension only were acting. That is, to a first approximation the effect of the hydrostatic pressure in producing rupture could be ignored. This is just what would be expected, because obviously if we imagine every atom exposed to additional forces directed radially at it and symmetrical from all sides, in addition to the forces which actually act on it, the superposed set of forces will be without effect on stability. To a first approximation, the effect of hydrostatic pressure is to superpose an additional system of forces of this character. But there are at least two factors which prevent this from being more than a first approximation. In the first place, an atom is not uniformly surrounded by neighbors on all sides, but the neighbors are situated at discrete points and so can only approximate a spherically symmetrical field. The approximation to a spherically symmetrical field is particularly crude at flaws. In the second place, when the structure is compressed, the atoms do not carry with them their original force fields undistorted (as is so often assumed in many approximate theories, and as we assumed above in our discussion of Poisson's ratio), but there is a distortion of the atomic force field which may have its own specific effect on the stability conditions. It is the combination of these two factors which determines the pressure coefficient of tensile strength, etc.

VII

Recently I have observed other kinds of fracture in connection with high pressure, and these have been so striking as to start me thinking again on this whole question of rupture, and to be the immediate occasion for this paper. The first example is that of a thick walled cylinder of hardened steel which was exposed to sufficient pressure on the outside to produce radial flow toward the center with permanent decrease of the diameter of the inside hole. On release of pressure, and after standing for some hours, a radial crack developed, starting at the inner wall and gradually working its way outward until it had practically reached the outside. The paradox in this situation is the development of rupture on *release* of the pressure that had produced the conditions of rupture. I had observed similar cracks in tubing collapsed by external pressure many years ago[6] but had not then observed the gradual growth of the crack in time. It is natural to say "internal strains and internal stress" in connection with situations like this, in which a material has been previously subject to plastic deformation, but the mere words are not sufficient unless detailed examination shows that the internal stresses and strains are in the right direction. An exact specification of the distribution of strain after release of stress is at present impossible because we do not have sufficient knowledge of the general behavior of the material in the plastic range, but a rough qualitative picture is suggested by the known solution in the elastic range. From this point of view it seems plausible that after release of external pressure there should be a circumferential component of tensile stress in the inner layers, and a corresponding circumferential compression in the outer layers. The inner tension and the outer compression must always, no matter what the wall thickness, be related by the equilibrium condition that the integral along the radius of the tensile stress exactly balances the radial integral of the compressive stress. It is therefore not impossible to imagine that on first release of pressure the crack starts at the inner wall because of a high circumferential stress of tension at this point, but it is impossible to suppose that the crack spreads all the way to the outside under the action of this same tension, because this would demand in the final thin layer that separates the end of the crack from the outside surface a highly anisotropic distribution of tension and compression. If, however, one gives up the demand that rupture requires the presence of a certain stress component in the direction of rupture, the whole situation becomes understandable enough when one reflects that on release of external pressure there is a circumferential *extension* throughout the whole mass. Rupture occurs if this extension exceeds the limits within which stability is possible. The zero from which the significant extension should be calculated is obviously the configuration reached by plastic flow at the

maximum external pressure. During plastic flow some lines of atoms must be crumpled and others extended, and some of the atoms permanently transported to new atomic environments. It is therefore not pertinent to consider that these atoms were once somewhere else, that is, to figure the strain from the initial configuration. Rupture under such conditions may thus occur on *release* of external load because by release of load a configuration is produced too far removed from the position of stability.

The *amount* of plastic flow produced at the maximum pressure and responsible for rupture on release of pressure may be so small as not to be easily measurable. Thus I have observed many times, in closed glass cylinders with thick walls which have been exposed to the action of heavy external pressure, spontaneous fracture after release of pressure on the lapse of several days. There was no measurable change of dimensions after such exposure to pressure, but the mere fact of spontaneous rupture is itself peremptory evidence that some permanent change had taken place.

The precise meaning to be attached to internal stress and strain in these situations evidently requires some analysis. The implication of the "internal" in these designations is that the external surface of the body is free and that one part of the body is acting against another. But we cannot define the internal stress in terms of the surface conditions unless we have knowledge of the properties of the body sufficient to enable us to integrate the stress-strain relations throughout the interior, and this we practically never have. We are driven to more indirect and hypothetical definition. Internal stress is comparatively easy to deal with—to find the internal stress at a point we may imagine a small piece of the body separated from the rest and find the forces which must be applied to the surface of this piece in order that its geometrical configuration shall be the same as when it was in its original position in the body. This is adequate to give unique meaning to the internal stress because it is known that the stress throughout the interior of a body is uniquely determined by the forces acting across the surface, independently of the elastic constants or other physical properties of the body, provided that the body is so small that the internal state of affairs can be treated as homogeneous. Whether the small piece of the body is actually reduced to the dimensions which it occupies in its original position must of course be determined by indirect means, such, for example, as by finding whether all such pieces into which the body can be imagined to be divided fit together so as to give the observed external shape to the body as a whole. This procedure for giving meaning to "internal" stress is the same as that for giving meaning in general to "stress at a point," and is unaffected by the previous history of the material or the stress in other parts.

The internal strain at a point in a body is not so easy to deal with as the internal stress because of the complication of determining the appropriate zero from which to calculate the strain. We may, of course, calculate the strain from the initial configuration or from a condition of zero stress, but the results obtained by such definitions would have only a geometrical significance, and would not be especially revealing as to the internal state of the body. One can see this by reflecting that in reaching its actual configuration from its initial configuration lines of atoms are crumpled or otherwise permanently distorted, or that in releasing the element to a state of zero stress the element may rupture. In fact, the concept of internal strain does not seem to be a particularly valuable one when one is so far from the initial configuration that permanent alterations have been produced. But if one is so near the original configuration that all deformations remain within the elastic range, then internal strain becomes a useful concept, and it may be given simple experimental meaning, as in the case of transparent bodies by optical procedures.

We have been using the words "stress and strain" in the technical sense in which they occur in the equations of elasticity theory, and we have already seen that in this sense they have meaning only from a large scale point of view. But we have already remarked that the words, particularly "strain," are often used in a less precise sense, which may give rise to confusion. In this less precise sense a body is said to be strained, or internally strained, if the atoms are in any sort of unnatural position which they tend to leave automatically. Such situations are very common, particularly in crystalline materials, as shown by the

frequency with which recrystallization occurs after plastic flow. One may suspect that atomic rearrangements less complete than actual recrystallizations are very common, and that they may be easily initiated by a change in the external conditions. Atomic disarrangements are evidently capable of an almost unlimited complexity, and it is impossible to describe them with a few simple parameters. It is to be expected that fractures are often initiated at such disarrangements. It is evidently important to distinguish between large scale strain or strain proper and this sort of small scale strain, because when attempts are made to formulate conditions of rupture in terms of stress and strain it is the large scale strain which enters the formulations, whereas it is really the small scale strain which is operative.

A very beautiful example of rupture on release of pressure and also against the stress is afforded by some recent experiments of D. T. Griggs.[5] In these experiments he studied, among other things, the compressive strength of limestone as affected by a hydrostatic pressure, acting over the entire surface of the body, superposed on the compressive load. Very large effects were found—under high hydrostatic pressure a very much greater compressive load is required to crush limestone than is required at atmospheric pressure (600 percent more under 10,000 kg/cm^2 hydrostatic pressure), and before fracture very considerable plastic deformations in compression occur, whereas at atmospheric pressure the material is brittle. Griggs found in many cases that if the experiment were terminated by release of compressive load and then release of pressure before the occurrence of compressive rupture, but after considerable plastic flow had taken place, the specimen was found, on removal from the apparatus, to be ruptured into discs on planes perpendicular to the original direction of compression. Although this sort of fracture was observed many times, Griggs for some reason did not describe it in his paper. The conditions in this experiment are particularly simple because the stress and deformation are homogeneously distributed throughout the mass. In particular, the component of stress across the plane prependicular to the axis of compression must be constant through the mass and must be equal to the compressive force acting across the ends. This stress, therefore, is always a compressive stress, except at the moment of release, when it becomes zero. At no time can there be a tensile stress in any direction. In spite of the fact that the conditions on the stress are about as clean cut and unequivocal as it would be possible to devise, I think that many persons on seeing these fractures will find it difficult to resist the temptation to say "It pulled itself apart," so strong is the appeal of the old intuitive point of view.

It is not difficult to see what must have happened in this experiment on limestone. During release of compressive load and hydrostatic pressure there is an extension of the body reckoned from the configuration which it had reached by plastic flow under the maximum load. This extension is greatest, of course, in the direction of the axis of compression. As long as the pressure is high, this extension takes place stably, because the atoms are still in sufficiently close contact in all directions. But when the pressure is reduced far enough, the corresponding extensions can no longer take place stably and the body ruptures across the planes on which the extension is greatest.

The suggestion given by this example prepares us to expect many other examples of rupture on *release* of a state of stress which has been preponderantly compressive, but in which there have been sufficiently large differences between different components of stress to produce permanent deformations. Such conditions are not common in ordinary testing; if they had been more common we would not have our intuitive feeling that fracture must be produced by a corresponding component of stress. Although such conditions are not common in every day experience, they are nevertheless not infrequent. All through my high pressure experimenting I have been continually bothered by fractures that occurred during *release* of pressure. Or there is another sort of experience that many people must have had. Like other experimenters, I have made many attempts to form coherent bodies for compressibility or other measurements by compressing the powdered material into a cylindrical mold between pistons. Although some substances can be successfully molded in this way, there are many others which invariably fall apart on removal from the mold

into disks, sometimes very thin, perpendicular to the axis. It is not necessary to argue after the analysis above that there can be no tensile *stress* producing these ruptures; it is sufficient to observe that on release of pressure there is an elongation in the direction of the axis. This elongation is obviously accentuated by the constraint exerted by the walls of the mold during release.

Obviously the field, *par excellence*, in which to look for effects of this sort is geology. Many rocks have been plastically deformed at great depths, and then brought to the surface with release of mean stress. One would expect fractures of this sort to be common. It may, however, not always be easy to tell by mere observation of the fractured material that fracture must have been produced in this way. But there are examples in which this mechanism can be observed in actual operation. It is known that quarrying operations are often accompanied by fracture of the rock with extensions.[7]

VIII

In conclusion and summary, the problem of rupture is essentially a problem in stability; this has been too little appreciated in mathematical deductions of the conditions of rupture. The difficulties of a complete mathematical discussion of the conditions of stability seem at present to be prohibitive. But in any event it would seem that local irregularities, if of the right sort, may be expected to be important in initiating instabilities. The important part played by internal "Lockerstellen," or by surface imperfections, in the rupture of actual materials is therefore not surprising. Much of the recent work by various authors in discussing the conditions of rupture is thus of great value and applicable in many situations of practical importance. But I think that if one contemplates the whole field of all possible conditions of stress, and in particular the almost infinitely complicated atomic rearrangements that occur in plastically deformed material, one feels the need for the utmost generality of analysis. In particular, one would not expect any general criterion of rupture in terms of the large scale stress and strain of ordinary elasticity theory. The stability of every atom is determined by its position with respect to its neighbors; when its position relative to its neighbors is changed, as by the application of forces to the surface of the body, its stability will change also. Changes of relative position making for instability may be of various types. In this discussion the importance of one particular type has been especially dwelt on, namely, unusual extensions in particular directions and the corresponding rupture by separation of fibers. It is not intended to suggest that under proper conditions the accompanying shearing distortion may not result in a corresponding instability. The deleterious effect of relative extensions probably tends to be less when the substance is on the average in a compressed state, with the mean force between the atoms repulsive instead of attractive. Very roughly, it seems to be the extensions reckoned from a state of uniform compression which are the major factor in initiating this kind of instability. This appears not unreasonable. Cases occur, in substances elongated in one or more directions, of rupture with no corresponding stress component or of rupture against the direction of total stress. On release of mean pressure from substances plastically deformed under the action of stresses which are on the average compressive, elongations will occur, calculated from the configuration reached at the maximum pressure, which is the proper zero to use, and ruptures may therefore be expected on *release* of pressure and *against* the stress. Various examples of this sort of thing have been found.

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Here and There

New Appointments and Promotions

Dr. Vannevar Bush has resigned as Vice President of the Massachusetts Institute of Technology to become president of the Carnegie Institution of Washington.

★

Dr. Allan C. G. Mitchell, chairman of the Department of Physics at New York University (University Heights), has been appointed head of the Department of Physics at Indiana University.

★

The Evening Star, Washington, D. C., states that two joint resolutions for appointment to the Board of Regents of the Smithsonian Institution, other than members of Congress, were introduced on June 7 by Chairman Keller, of the House Library Committee. One provides that R. Walton Moore, solicitor of the State Department, shall succeed himself for the statutory term of six years after June 29. The other would fill the vacancy caused by the death of Augustus P. Loring by appointment for the six-year term of Dr. Arthur H. Compton, Professor of Physics at the University of Chicago.

Science, June 17, 1938

★

Dr. W. L. Bragg, Cavendish Professor of Experimental Physics in the University of Cambridge, has been elected Professor of Natural Philosophy in the Royal Institution, London, in succession to the late Lord Rutherford. Professor Bragg is the son of Sir William Bragg, Fullerian Professor of Chemistry and Director of the Royal Institution.

★

Dr. Elmer O. Kraemer has resigned as a member of the experimental staff of the duPont Company at Wilmington, Delaware, a position which he has held since 1927. He has received from the Lalor Foundation an award of $2500 to facilitate the continuance of his studies of the size and shape of giant molecules. His investigations will be carried out at the University of Uppsala in the laboratory of Professor The Svedberg. He also plans to visit the principal research centers for physical and colloid chemistry in Europe.

★

The Order of Merit was conferred on Sir Arthur Stanley Eddington, Plumian Professor of Astronomy at the University of Cambridge and Director of the Observatory.

Tribute to Max Planck

The recent issue of the *Annalen der Physik* has been dedicated to Professor Max Planck in honor of his eightieth birthday on April 23.

★

Duddell Medal Award

The Council of the Physical Society has this year awarded the fifteenth Duddell Medal to Professor Hans Geiger, of the University of Tubingen. The medal is awarded to "persons who have contributed to the advancement of knowledge by the invention or design of scientific instruments, or by the discovery of materials used in their construction."

★

Lamme Medal Award

The Society for the Promotion of Engineering Education recently presented the Lamme Medal for achievement in this technical field to Robert Lemuel Sackett, Dean of the School of Engineering at Pennsylvania State College from 1915 to 1937.

★

A.S.T.M. Organizes New Committee on Radiographic Testing

Since the Symposium on Radiography and X-Ray Diffraction Methods sponsored by the American Society for Testing Materials in 1936, there has been evident an increasing interest in the need for research and standardization work on important problems in the field of radiographic testing. In order to carry out work in this field the Society has organized a new committee designated E-7 on Radiographic Testing. The new committee will extend phases of the work heretofore carried out by Committee E-4 on Metallography. Under the leadership of Dr. H. H. Lester, Watertown Arsenal, who was asked to take charge of developing preliminary plans for the committee, the committee was formally organized on February 14 at a meeting held in New York City, at which a large number of those invited to serve on the committee were present. There was also a meeting held during A.S.T.M. Committee Week in Rochester.

★

Necrology

Dr. William Wallace Campbell, Director Emeritus of the Lick Observatory and President Emeritus of the University of California, died on June 14.

Research on Sun's Energy

The Massachusetts Institute of Technology has received a gift of $647,700 from Dr. Godfrey L. Cabot, of Boston. The income from the gift, which will be known as the Solar Energy Fund, will be devoted specifically to a search for direct methods of converting the sun's radiant energy into useful power or storing such energy for future use. These investigations will be continued for at least fifty years, after which the fund may be used for such other purposes as the corporation of the institute may select. To assist in the direction of these investigations, the following committee has been appointed: Professors Hoyt C. Hottel, Department of Chemical Engineering; Arthur C. Hardy, Department of Physics; Ernest H. Huntress, Department of Chemistry; Arthur R. von Hipple, Department of Electrical Engineering and George W. Swett, Department of Mechanical Engineering.

★

Symposium on Plastics

The American Society for Testing Materials, through its Committee D-20, sponsored a Symposium on Plastics at its March Regional Meeting comprising six technical papers with considerable discussion. These papers are published in a 51-page booklet which can be obtained from the American Society for Testing Materials, 260 S. Broad Street, Philadelphia, Pa.

★

Calendar of Meetings

Acoustical Society of America
Cambridge, Mass., November 18–19, 1938

American Association for the Advancement of Science
Richmond, Va., December 28–31, 1938

American Association of Physics Teachers
Washington, D. C., December 27–30, 1938

American Physical Society
Chicago, Ill., November 25–26, 1938
Los Angeles, Cal., December, 1938
Washington, D. C., December 26–28, 1938
New York, N. Y., February 24–25, 1939

Optical Society of America
Niagara Falls, Canada, October 27–29, 1938

Society of Rheology
Pittsburgh, Pa., December, 1938

Among Our Authors

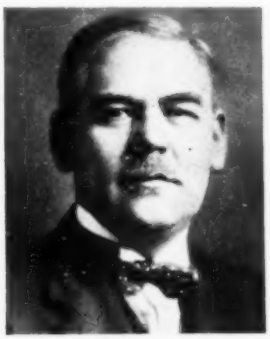
Dr. S. S. Sidhu received his B.S., M.S., and Ph.D. degrees from the University of Pittsburgh. He was research engineer with Union Switch and Signal Company, 1928–1932, Professor of Physics at North Braddock Junior College, 1933–1937 and from 1937 to date he is physicist in charge of the Cooperative X-Ray Laboratory of the University of Pittsburgh.

Dr. Percy W. Bridgman received his A.B., A.M. and Ph.D. from Harvard University in 1904, 1905 and 1908 respectively. He was a Fellow and an assistant in Physics at Harvard from 1908 to 1913; an assistant professor from 1913 to 1919, and professor from 1919 to 1926. Since 1926 he has been Hollis Professor of Mathematics and Natural Philosophy.

Mr. D. W. Glaser, who is 29 years old, was born in Minneapolis, Minnesota. He received the Master of Science degree in Chemical Engineering from the University of Minnesota in 1935. He has been chemist for the Glidden Paint Company at Minneapolis since 1929.

Dr. Eli Franklin Burton received his B.A. and his Ph.D. degrees from the University of Toronto in 1901 and 1910, respectively. He was a fellow at Toronto from 1901 to 1903; from 1904 to 1906 he was an 1851 Exhibition scholar at Cambridge; from 1906 to 1911 he was senior demonstrator at Toronto; an associate professor there from 1911 to 1924; and from 1924 Professor of Physics. Since 1932 he has been head of the Physics Department and Director of the McLennan Laboratory.

P. W. Bridgman



E. F. Burton

S. S. Sidhu

Some of the New Books

Science and Music. SIR JAMES JEANS. Pp. 258+x, Figs. 64, 14½×22 cm. The University Press, Cambridge and the Macmillan Company, New York, 1937. Price $2.75.

It is always useful to have a list of good semi-popular books on science on hand, to give lay questioners as references for further details. It saves one's voice, and often enlightens and interests the layman more than haphazard discussion with an expert would. The new book of Jeans will be a good one to add to your reference list under the headings of acoustics and music; it probably will be a popular one.

It is a much more difficult task to write an interesting popular book about the older, better-known branches of physics than it is to catch the public's eye with elucidations of the mysteries of relativity and quantum mechanics. This former task is in the reviewer's opinion more difficult, not because the subject matter is more abstruse, but because the average reader is less interested in a subject about which he has some information (even though it is false) than he is in one which is completely unknown to him. Jeans has long shown an aptitude for clarifying modern physics to the layman. He now has written a book on sound which is the equal of his earlier books, since it contains a high percentage of correctly stated facts and is readable enough to make up for the lack of mystery of the subject.

He has wisely left out any discussion of the complicated details of the electrical aspects of modern sound technique, and has concentrated on the purely acoustical aspects of the science, those parts with which the musician and the musically-minded layman should be acquainted. The subject matter starts off with a quite lucid discussion of simple harmonic vibrations, of periodic vibrations in general, and of the superposition of such vibrations. The next chapter discusses the vibrations of strings, the harmonic or Fourier series, and the analysis of musical sound into such a series. There is an interesting analysis of the vibrations of plucked, struck and bowed strings, and a discussion of the properties of pianos and violins. Next comes a chapter on vibrations of air, including discussions on edge tones and on wind instruments.

The next chapter, on harmony and discord, also touches upon the fundamental difficulties in the choice of musical scales, that perennial source of argument among musical theorists. The last two chapters are on two branches of acoustics which should be as familiar to the musician as the principles of harmony: the acoustical properties of rooms and of the human ear. There is a good discussion of reverberation and of the usual method of calculation of reverberation time. And finally there is a report on the range and limitations of the human ear as a receiving instrument.

The book has a short but probably adequate index, and is well illustrated with line drawings and with a good selection from the ever-useful collection of sound wave photographs taken by Professor Dayton C. Miller with his phonodeik.

This book of Jeans, giving the point of view of a scientist interested in music, is a satisfactory supplement to *Music, a Science and an Art* by John Redfield, where is given the point of view of the musician interested in science. Both books can be recommended to the interested laymen who has a fear of the mathematics usually present in books on sound; and both should be required reading for those seriously interested in music.

PHILIP M. MORSE
Massachusetts Institute of Technology

Photoelements. B. LANGE, translated by ANCEL ST. JOHN. Pp. 297, Figs. 167. Reinhold Publishing Corporation, 1938. Price $5.50.

This work is an English translation of Dr. Lange's *Die Photoelemente und ihre Anwendung*, which was published in two parts in 1936 and favorably reviewed in the Physikalische Zeitschrift **37**, 352 (1936); **38**, 735 (1937). It deals with the barrier-layer photovoltaic cells which have attracted increasing notice during the past few years owing to their ability to transform radiant energy into electrical form suited to operate indicating devices directly without the necessity of using amplifiers or auxiliary sources of power.

Part I opens with a history of photovoltaic cells. Accustomed as we are to think of them as recent developments, it is interesting to read that C. E. Fritts produced a practical dry-type selenium photovoltaic cell well over fifty years ago and published data showing clearly its potential usefulness as a rectifier of alternating currents. This experimental work was not followed to commercial application at that time, however, and the essential phenomena were re-discovered before the recent development began.

The experimental results on semiconductors and the interpretation of these results are discussed quite fully and should prove especially interesting to workers in other fields. The apparently unrelated observations of the Becquerel effect, the crystal photo-effect and the barrier-layer photo-effect are shown to differ only externally and their fundamental identity with the basic photoelectric process is clearly set forth. The theories and physical properties of these "semiconductor photo-cells" are reviewed in detail and the ageing and fatigue effects are discussed.

Part II gives practical information on the structure of modern photovoltaic cells and lists, with detailed descriptions, a large number of applications in the most diverse fields of scientific and industrial work.

Although the English style makes the reader conscious that the text is a translation, the thought is clear and coherent. Extensive bibliographies are given at the end of each part of the work.

L. T. BOURLAND
Westinghouse Research Laboratories

Elektronen-Roehren, 4. Band: Gleichrichter und Empfänger. (Electron Tubes, Vol. 4: Rectifiers and Receivers.) HEINRICH BARKHAUSEN. Pp. 294, Figs. 147. S. Hirzel, Leipzig, Germany. Price RM 9.00.

Dr. Barkhausen, discoverer of the ultra-high frequency oscillations which bear his name, is well known to scientists and engineers in this country as Professor and Director of the celebrated Institut für Schwachstromtechnik of the Technische Hochschule at Dresden.

This volume is the last published addition to Barkhausen's *Manual of Electron Tubes*. Previous volumes have dealt with general fundamentals, amplifiers, and regeneration. This volume dealing with rectifiers and receivers maintains a clean cut distinction between rectifiers proper and their use as detectors. A third section on present day German receivers is added with the hope that the art has reached a reasonable state of permanence.

The first section dealing with the action of rectifiers and detectors when the applied alternating voltage is unmodulated gives a detailed development of diode theory. It is probably safe to say that this treatment is the most detailed and extensive which has ever appeared in print. The development considers the diode action from all angles and makes extensive use of mathematical and graphical analysis. The complete characteristics are derived and given in tabulated and graphical form for three ideal diode characteristics, i.e., linear, parabolic, and exponential characteristics. Triode detector action is presented as a natural extension of the diode behavior.

The second section applies the theory of the first to the actual response of detectors to modulated signals. This is introduced by a section on circuit theory with a discussion of side-band theory, the analysis of an interrupted alternating current, and a brief treatment of "frequenz modelung." Included in this is an original treatment of the frequency discrimination and band width of coupling circuits. Concerning the actual operation of tubes emphasis is placed upon the practical limitations which cause the operation to diverge from that predicted by the theory in the ideal cases. Every possible type of operation is considered. An analysis is given of diagonal clipping and negative peak clipping in diode detectors. The effect of nonlinearity of triode characteristics in producing cross modulation is similarly treated. The section concludes with a general treatment of frequency transformation.

The third section is a critical study of some typical receivers. Actual data on the construction of these receivers is given together with a detailed circuit diagram of each. The types studied are a tuned radiofrequency receiver, a super-heterodyne receiver and the celebrated Volksempfänger (regenerative detector and amplifier). A discussion is given of the relative merits of these receivers from the standpoint of their selectivity, sensitivity, and fidelity.

This volume, No. 4 of the *Manual* is written in a clear and crisply precise style. Characteristically, no bibliography is included. As the author slyly remarks, a complete bibliography encompassing the world literature would require a fifth volume to the series, one less extensive would be almost useless. This departure from conventional procedure is justified by the way in which the author uses fundamental notions as a starting point for all ideas developed. The book is in every sense complete in itself.

From the standpoint of the originality and completeness of treatment Volume 4 is probably the best volume of the *Electron Tube Manual*. The book will be a valuable addition to the library of American radio engineers, particularly those interested in the theory and actual operation of modern detectors.

KARL SPANGENBERG
Stanford University

Engineering Electronics. DONALD G. FINK, Managing Editor, *Electronics*. Pp. 358, Figs. 216, 15×23 cm. McGraw-Hill Book Company, New York, 1938. Price $3.50.

To those interested in modern technology this book will prove most interesting reading. To the practicing engineer who has not had specific training in this important field, much will appear that is helpful and instructive.

It is designed primarily for the needs of this class of reader and involved theoretical discussions are avoided throughout as well as the use of mathematics more advanced than high school algebra and trigonometry. The explanations of electronic phenomena are exceptionally clear and are logically carried forward from step to step.

The introductory chapter outlines the enviable position electronics enjoys in modern engineering practice. Numerous examples are cited.

The next four chapters designated as Part I discuss at some length the fundamental properties of the electron, the methods by which they may be produced in the free state, how they may be controlled and finally, a general idea is given of their behavior in the presence of rarefied gases and vapors.

Part II deals with the construction, principles of operation and characteristics of electron tubes. Thermionic vacuum tubes, gas-filled tubes, photosensitive tubes and electronic sources of light are discussed. Chapter X deals with specialized electron tubes such as the cathode-ray tube, the iconoscope, the various electron multipliers and the strobotron.

An introduction to a.c. circuit theory irritates the section devoted to a discussion of the various ways in which the electronic tubes described in Part II may be usefully employed. This study is grouped under power transformation, communication, and methods of industrial control and measurement.

Owing to the quantity of material upon which the author has endeavored to report there are numerous points which might well be more fully treated. This objection is met however by a fairly comprehensive list of reference books and articles to which the inquiring reader may go for more detailed information.

Such equations as are used are employed in simple illustrative problems which serve also to emphasize and clarify the author's point.

Some of the more technical discussions of tube design leave something to be desired from the standpoint of accuracy. For example he states that the Tungar or Rectigon tube contains gas "at pressures comparable with atmospheric pressure (760 mm)." The tube engineer will probably take exception to certain other explanations of the whys and wherefores of tube design. It is the writer's opinion however, that these inaccuracies do not detract appreciably from the value of the book. Numerous problems are offered for solution and *mirabile dictu*, the answers are supplied in the closing pages.

It is a book well worth having.

E. F. Lowry
University of Chicago

Light. Vivian T. Saunders. Assistant Master at Uppingham School, England. Pp. 328, Figs. 196. Chemical Publishing Company of New York, 1938. Price $2.50.

This book covers the usual content of a first course in optics in an admirable manner. The presentation is interesting, clear, and logical. The derivations are carried through in full detail with an explanation of every assumption and approximation. By good example, this should give the student a conception of precise thinking. Frequent references to early writings and to everyday observations stimulate the reader's interest and provide a cultural background. The illustrations are numerous and good, though they are not always in the most convenient place for ready reference as one follows the text. There are many problems at the end of each chapter and the results are given at the end of the book. The scope of this text is indicated by the omission or bare mention of the following topics: interference in polarized light and its applications, x-ray spectra, the photon theory of light, and the Michelson interferometer.

Joseph Valasek
University of Minnesota

Innovations in Instruments

Hand Tachometer

The most striking feature of this new instrument is that it measures any speed from 30 r.p.m. up to 40,000 r.p.m. with only three tachometer ranges. It is equivalent in speed coverage to former six-range hand tachometers. This is done by allowing the indicating pointer to make two turns around the dial instead of one, thereby making the scale 13 inches long. One advantage is that a wide variation in speed can be observed, such as from 300 to 4000 r.p.m., without stopping to change the range.

The "Jagabi" *Universal* hand tachometer operates on the same centrifugal or fly-ball governor principle as James G. Biddle Co.'s type C tachometers, but has been redesigned to include ball-bearings, a knife-edge pointer, a rotating gear shift and other refinements. The indicating dial is 3 inches in diameter. The shape, size and weight are such that it fits snugly and firmly in the hand, so that the operator is insured a firm and steady grip, which is essential in using any tachometer. The instrument is supplied complete with carrying case and accessories. Two ratings are available: 30 to 40,000 r.p.m. and 25 to 30,000 r.p.m.

Automatic Voltage Stabilizer

A Raytheon voltage regulator permanently corrects the varying voltage conditions that are generally encountered and provides the constant a.c. voltage so essential for the effective operation of many electrical devices. Since the regulator will stabilize at any load within rating, it may be used as an accessory to devices already installed. Some of the types of equipment which are benefited by a stabilized voltage are x-ray machines, color comparators, photo-printing devices, photometers, and amplifiers used in talking motion pictures, radio transmitters, and telephone apparatus. It is also widely used by laboratories making electrical experiments and for general use.

A typical Raytheon voltage regulator stabilizes an a.c. voltage that may be varying from 95 to 130 volts and holds it constant at 115 volts plus or minus 1 percent automatically and instantaneously. It is a magnetic device

without moving parts or adjustments. It can be made to operate from any commercial a.c. power source and deliver one or more required voltages with power outputs up to several thousand voltamperes. Bulletin DL48-71-F has been prepared to give full information and electrical characteristics, dimensions, stock ratings and prices. It contains illustrations and examples of how to select voltage regulators for specific applications and for general use. Copies will be mailed on request. Address Raytheon Manufacturing Company, 156 Willow Street, Waltham, Massachusetts.

★

Rectifier for Arcs

A great many measuring and inspection machines used in factories and laboratories have as a light source arc lamps that use 6 millimeter carbons. These lamps will operate on a.c. or d.c. but d.c. operation is preferred because it results in the brightest possible image on the screen. It is a characteristic of a d.c. arc that it is most intense at one small spot on the negative carbon and this makes it easy for the operator to align the light source on the optical axis of the projector and maintain a steady,

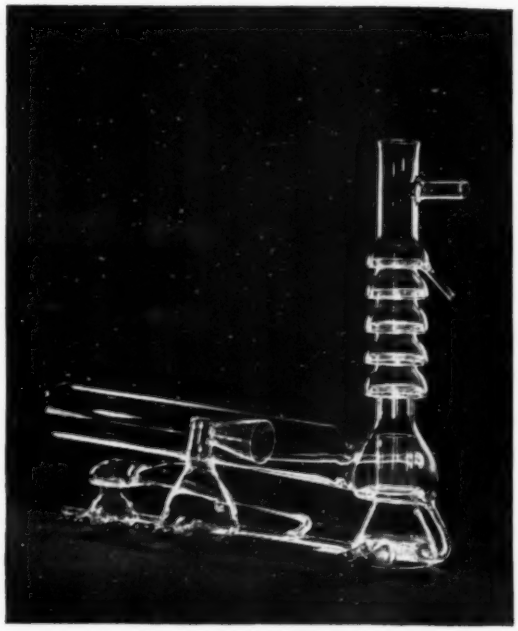
continuous arc. There also is the advantage that the arc strikes quickly and is maintained easily, free from sputtering and troublesome interruption.

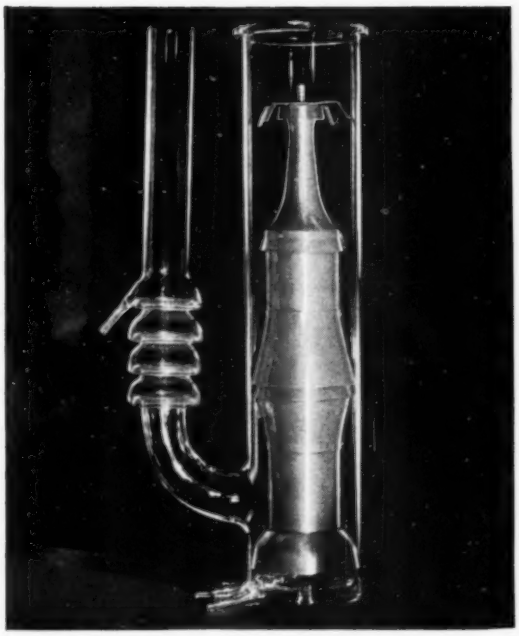
To provide d.c. of the proper characteristics for all makes of 6 millimeter carbon arc lamps a Raytheon rectifier has been designed to convert 115 volts a.c. to 60 volts, 5 amperes d.c. An illustrated bulletin has been prepared giving prices and a full description which may be obtained by writing Raytheon Manufacturing Company, 156 Willow Street, Waltham, Massachusetts, and requesting bulletin DL48-237.

★

New Oil Diffusion Pumps

The Eastman Kodak Company announces two high vacuum oil diffusion pumps which will interest physicists. One of these is an all glass pump so designed that purification of the oil takes place during operation. It is useful where extremely high vacuum is required. Using the oil "Octoil" a pressure of 5×10^{-6} mm may be obtained. The other pump is constructed of both glass and metal and is designed for the rapid evacuation of large chambers which occur in cyclotrons, vacuum spectrographs and in metal sputtering outfits. Both pumps are cooled by air and are furnished with electric heaters.





Contributed Original Research

The Reflection Coefficient of Mercury

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Research Laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pennsylvania
(Received January 19, 1938)

Two new methods for measuring the reflection coefficient of mercury atoms from a mercury surface are described. In the first, a micromanometer gives both the change in pressure on the surface, and the subsequent rate of evaporation, when a mercury pool is exposed to an opposing liquid air cooled condensing target. From these, reflection coefficients from 0.93 to over 0.99 are obtained. In the second, from measurement of the vapor density between evaporating and condensing surfaces by an ionization gauge, the reflection coefficient can be calculated. With careful purification of the mercury, quite small reflection coefficients result, a mean of 0.2, and a minimum of 0.07 being found. Exposure of the mercury surface to the atmosphere for half an hour brings the reflection up to 0.8, while after 10 days' exposure the reflection coefficient becomes 0.92.

THE familiar kinetic theory deduction of the maximum rate of vaporization of a substance proceeds from considering a liquid or solid surface in equilibrium with its vapor: let the number of atoms striking the surface per sq. cm per sec., from the gas phase be $\nu_i = n_i \bar{u}_i$, where n_i represents the density of atoms in the gas with velocities directed toward the surface and $\bar{u}_i$ is the mean of those velocities. Similarly, we may denote the number of atoms traveling away from the surface per sq. cm per sec. by $\nu_0 = n_0 \bar{u}_0$. In equilibrium, of course, $\nu_i = \nu_0$. If an experiment can be suitably arranged so $\nu_i = 0$, without any change in the temperature or character of the surface, and if ν_0, can be considered to have its value unchanged, then ν_0 will give the rate of vaporization of the surface into a vacuum. Kinetic theory then will give $\nu_0 = P/(2\pi mkT)^{\frac{1}{2}}$, where P is the equilibrium vapor pressure of the material.

Now if an experimentally measured rate of vaporization is less than the above ν_0, the discrepancy may be explained through a reflection coefficient. If a fraction r of the atoms striking the surface are reflected, and only $(1-r)$ condense, then in equilibrium ν_0 is composed of $r\nu_i$ reflected atoms and $(1-r)\nu_i$ atoms evaporated afresh to replace those condensing, so again $\nu_0 = \nu_i r + \nu_i(1-r) = \nu_i$. The actual rate of vaporization is thus $(1-r)\nu_i = (1-r)\nu_0$ and this last should be the measured rate when $\nu_i = 0$.

From measured rates of vaporization from a mercury surface a wide range of reflection coefficients have been reported in the literature. Knudsen[1] found coefficients from $r > 0.9995$ for a discolored surface to r approaching zero for freshly formed drops; Bennewitz[2] reports $r = 0.9$ to 0.95 for commercially pure mercury, but after repeated vacuum distillations r became 0.35 to 0; Volmer and Estermann[3] observed r within a few percent of zero for a wide range of temperature; while Risch[4] from the difference in ν_i and ν_0, for mercury condensing on a wall obtained r initially 0.89 decreasing to 0.45 after repeated purification.

In all the above work, an accurate knowledge of the temperature of the mercury surface was extremely important, since the equilibrium vapor pressure, upon which the calculation of r depended, varies so rapidly with temperature: an error of 1° in temperature at room temperature, causes an error of 8 percent in vapor pressure

* Now at the University of Utrecht, Utrecht, Holland.

[1] Knudsen, Ann. d. Physik **47**, 697 (1915).
[2] Bennewitz, Ann. d. Physik **59**, 193 (1919).
[3] Volmer and Estermann, Zeits. f. Physik **7**, 1 (1921).
[4] Risch, Helv. Phys. Acta **6**, 128 (1932).

determination. If the pressure on the surface could be measured at the same time as the rate of vaporization, then this source of error would be eliminated. In equilibrium, the pressure on the surface, in dynes per sq. cm, in the same notation before used,

$$P_1 = n_0 m\overline{u_0^2}(1-r) + n_i m\overline{u_i^2}(1+r),$$

where m is the atomic mass. The r in the last term arises since the reflected atoms impart an equal momentum to the surface when they arrive and when they leave. When ν_i is made zero, the pressure becomes

$$P_2 = n_0 m\overline{u_0^2}(1-r).$$

The difference in the two,

$$\Delta P = n_i m\overline{u_i^2}(1+r). \tag{1}$$

The rate of vaporization, M, in grams per sq. cm per sec. is given by

$$M = m n_i \bar{u}_i (1-r). \tag{2}$$

Dividing (1) by (2) and adding a factor g to take account of the different units,

$$\frac{\Delta P g}{M\overline{u_i^2}/\bar{u}_i} = \frac{1+r}{1-r}. \tag{3}$$

In Eq. (3), a knowledge of the temperature is unimportant, since an error of 1° would cause only an uncertainty of 0.16 of 1 percent in $\overline{u_i^2}/\bar{u}_i$.

The Chattock micromanometer which had been modified for another purpose,[5] made it possible to measure simultaneously ΔP and M. Fig. 1 shows a sketch of the apparatus. The mercury surface investigated was contained in a heavy-walled, nickel-plated copper tube, which communicated with the micromanometer. A sliding lid, in good thermal contact with the tube, covered the surface or exposed it to the liquid air containing glass condensing target directly above. A bath around the tube permitted control of the mercury temperature. When the lid covered the pool, equilibrium existed, and a pressure corresponding to P_1 above was registered on the manometer, which was adjusted so this gave a suitable zero reading in the measuring microscope. Then the lid was opened by an external magnet, so all the mercury atoms striking the liquid air cooled target condensed. The pressure on the pool reduced to P_2, since with substantially no collisions occurring in the space above the pool, atoms traveled only away from the surface. The sudden change in gauge reading when the lid was opened equalled ΔP.

The micromanometer not only registered the

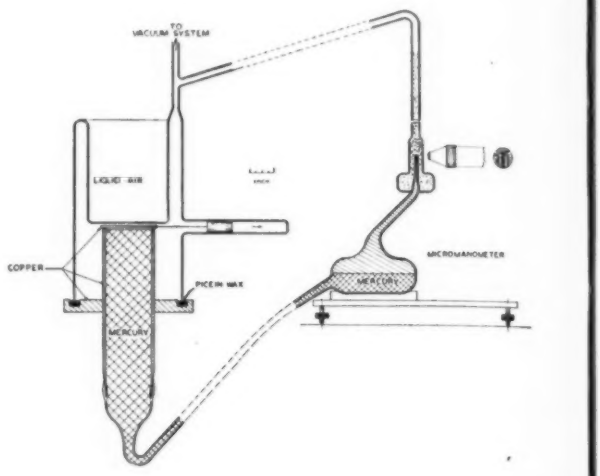

FIG. 1. Chattock micromanometer with some modifications.

force on the surface of the mercury pool, but also effectively *weighed* the mercury contained in the tube. With the lid open, the evaporation of mercury and condensation on the target resulted in a continual change in the deflection read in the microscope. The rate of change of deflection was, of course, proportional to the quantity M. Since both ΔP and M were read by the same instrument, it was not necessary to obtain the calibration of the instrument. The velocity in (3) was readily found from the temperature and hence r calculated.

Results for a typical test may be seen in Fig. 2, where the deflection of the micromanometer, in arbitrary units, is plotted against time. At first the lid covered the pool, so equilibrium existed. At $t=40$ sec., the lid opened and the gauge deflection decreased because the condensing target eliminated the atoms flowing back to the pool. Now after this, any evaporation reduces the head of mercury, and should be indicated by a continually decreasing gauge deflection. Actually, there occurred practically no change until at

[5] Mason, Phys. Rev. **47**, 241 (1935).

$t=160$, the lid was again closed, whereupon the original reading reestablished. No considerable evaporation could have taken place, but it is not possible to fix exactly the rate because of the extraneous disturbances which caused the actual increase in deflection during the time the pool was exposed to the condensing target. If the true rate is taken as less than the maximum spread in the readings while the valve is open divided by the time, then Eq. (3) gives $r>0.97$.

A further check on the reflection coefficient was secured by using the manometer as an absolute instrument rather than interpreting the relative readings obtained. The micromanometer was calibrated against a McLeod gauge by varying the air pressure in the system with the mercury pool uncovered and all parts at a uniform temperature. The temperature of the mercury surface was known fairly closely during an experiment from the temperature of the bath surrounding the tube. From the I.C.T. vapor pressure data, n_i appearing in Eq. (1) was found, so with the absolute determination of ΔP, r was calculated by this equation to be 1, within the limits of experimental error. If r had been zero, then calibration of the instrument showed that the deflection should have followed the dotted line in Fig. 2.

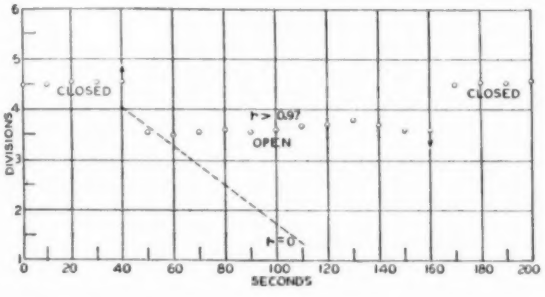

FIG. 2. Micromanometer deflection with mercury surface in equilibrium and evaporating. The words "open" and "closed" refer to the position of the trap door covering the mercury pool.

Extensive experiments with temperatures of the mercury pool between 20°C and 44°C gave values of r from 0.93 to over 0.99. In all cases, the mercury surface was clean and bright appearing to the eye. It is possible, however, that some surface contamination was present, as in the design of apparatus used, the mercury was poured in, without vacuum distillation, and then a glass and metal joint waxed together as shown in Fig. 1.

As the reflection coefficient turned out so large, the density of mercury atoms in the space between the evaporating and condensing surface was so extremely small that no appreciable number of collisions occurred in the gas space to hinder the evaporation of the liquid. Neither did the finite area of the mercury pool affect the accuracy of the results. Random changes in deflection of the micromanometer like those exhibited in Fig. 2, which might occur with the apparatus in equilibrium as far as controllable, were the chief sources of error. Because of the high sensitivity of the instrument, vibration and temperature changes within the room were troublesome. These limited the accuracy to less than the theory indicated might be expected from the type of measurements.

Another method of measuring the reflection coefficient, though less accurate in principle, but offering certain advantages, was devised in which an ionization gauge was used to measure the density of atoms between evaporating and condensing surfaces. In the previous notation, the total density of atoms when equilibrium exists is

$$\bar{n}=n_0+n_i=2n_0.$$

When evaporation alone occurs, $n_i=0$, and

$$\bar{n}'=n_0'=n_0(1-r)$$

so

$$\bar{n}'/\bar{n}=(1-r)/2. \qquad (4)$$

By measuring $\bar{n}$ and $\bar{n}'$, for the same temperature of mercury surface, the reflection coefficient may be obtained. Fig. 3 shows the tube in which this was done. A Kovar-tungsten thermocouple TC, just below the mercury surface, gave the temperature of the mercury. This distance between the mercury and the opposing glass surface which could be used for condensing was about 0.25 in. In this space was placed an open meshed ionization gauge, IG, constructed entirely of fine wires in order to minimize the retardation to flow of vapor through the gauge. First, with a suitable bath the temperature of the entire tube was brought into equilibrium, and the ionization

gauge and thermocouple read; then, with liquid air in the condensing target, the ionization gauge was read again for the same thermocouple voltage. The ratio gave directly the $\bar{n}'/\bar{n}$ of Eq. (4), without inquiring about the temperature distribution in the mercury pool, the calibration of the thermocouple, or the vapor pressure of mercury.

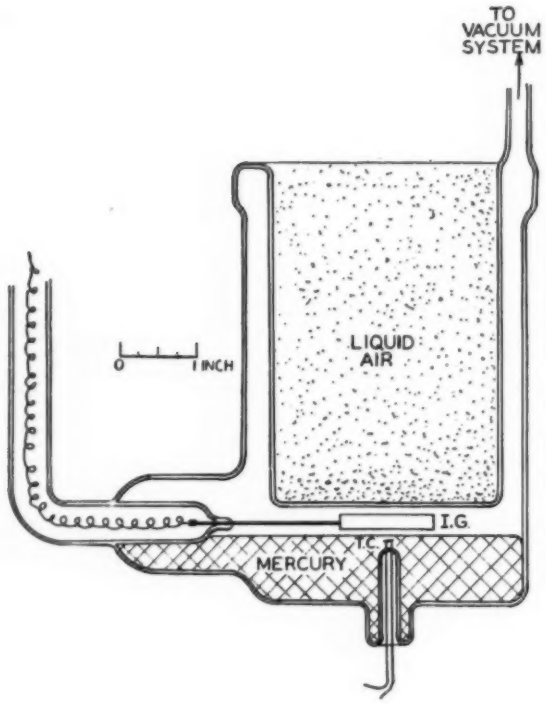

FIG. 3.

With a preliminary tube of design similar to Fig. 3, it was found that reflection coefficients from nearly 0 to almost 1 could be obtained, the lower values being secured soon after the tube was assembled, and the higher values after some days of testing under different conditions. In the present tube particular care was exercised to obtain clean mercury. The tube, made from G-702-P glass, was baked a total of 12 hours at 500°C, and briefly at 550°; the parts of the ionization gauge were well outgassed by bombardment. Liquid air was kept on a trap between the tube and the pumps. The pumps were run continuously.

The mercury used was triple distilled: first laboratory clean mercury was slowly distilled from one reservoir into a second, while the test tube and a third reservoir were baking at 500°. Then the mercury was distilled from the second reservoir into the baked out third reservoir, with the test tube at 400°. After 3 hours further baking at 500° of the test tube, the final distillation brought mercury to the proper level in the test tube. After each distillation the reservoir emptied was sealed off from the system.

Within an hour after the final distillation of mercury, the reflection coefficient was determined to be 0.25. After three days, r had decreased considerably, while in the next four days r increased again. During this latter period, different gases were admitted to the system, but no direct correlation between r and the gas introduced was found: the changes in r were no greater than those recorded under supposedly constant conditions. The maximum value of r found in this period was 0.32 and the minimum was 0.07.

The gases studied were allowed to stand over the mercury for chosen times, and then completely pumped out before the filament of the gauge was heated to measure r. Oxygen, up to 0.22 mm for 16 hours had no marked affect on r; neither did 0.05 mm of hydrogen for 1 hour nor 0.41 mm of air, which had been stored over P_2O_5 for several years, for 16 hours. But when room air at atmospheric pressure was admitted for half an hour and then pumped out quickly, the reflection coefficient *increased* from approximately 0.2 to 0.8. For two days thereafter, r remained substantially constant. Then the mercury was again exposed to the atmosphere for 10 days, after which r was found to be about 0.92.

Two sources of error enter with this method: first, the density of atoms near the gauge when condensation is taking place is limited by the finite area of the evaporating surface; second, through the effect of collisions, n_i will not be zero, so $\bar{n}'$ will be greater than n_0'. The first of these effects makes the r calculated by Eq. (4) greater than the true reflection coefficient while the second makes the calculated r too small. From the geometry of the tube, the first would cause an error in $\bar{n}'$ of only 7 percent if no reflection occurred from the outer glass walls above the mercury; the actual error must be less than 7 percent. For small r, the percentage error

in the reflection coefficient would be very large, however. The magnitude of the second depends, of course, on the vapor density. The ranges worked with correspond to mean free paths of approximately two to twenty times the distance between evaporating and condensing surfaces, for $r=0$; for $r>0$, the mean free paths would be correspondingly greater. An idea of the error may be secured from the variation of r with temperature: for the initial low reflection coefficients, the mean value of r for a thermocouple temperature of 28°C was 0.18, while for 8°C, the mean r was 0.25.

It has been assumed in the past that for clean mercury the reflection coefficient is zero. The experiments reported herein bear out this hypothesis. The amount of impurity necessary to produce almost complete reflection, however, must be very small, as values of r approaching 1 were found for surfaces quite bright and clean appearing. Quite possibly a monomolecular, or at least an extremely thin, layer of adsorbed substance suffices to change r greatly. The stringent care necessary to make r small indicates that in most practical devices using mercury, very large reflection coefficients may be expected.

Studies in Lubrication

II. Experimental Friction Coefficients for Thick Film Lubrication of Complete Journal Bearings

F. Morgan and M. Muskat
Gulf Research & Development Company, Pittsburgh, Pennsylvania
(Received April 29, 1938)

A straight line which, when extended, passes through the origin of coordinates is obtained when the coefficient of friction for a full journal bearing operating in the thick film region is plotted against $\mu N/P$, where μ is the lubricant viscosity, N the journal speed, and P the bearing load per unit of projected area. At higher speeds, when the film temperature around the bearing is not reasonably uniform, large deviations from this line are found. An increase of friction, which qualitatively confirms the theory developed in part I of this series, is observed when the strength of the source of lubricant is increased.

Introduction

In the first paper[1] of this series attention was called to the lack of agreement in many of the results of various experimenters as well as to the need for a satisfactory theory for practical cases of journal bearing lubrication. A theory, based upon a method of successive approximations, and valid for low values of the journal eccentricity, was presented for full journal bearings of finite length. Since the test of any adequate theory must lie in its agreement with experiment, the results of some experiments designed as a test for this theory will be discussed here.

In spite of the afore-mentioned discrepancies many experimenters seem to agree upon certain features of the problem. A brief summary of the past developments will be given in order that the results hitherto obtained may be kept in mind.

The experiments of Beauchamp Tower[2] are important in that they showed for the first time the action of the liquid pressure in a lubricating film, and proved that under favorable conditions the bearing surfaces may be completely separated and the friction not influenced by surface characteristics. These experiments formed the basis of the hydrodynamic theory of bearing

[1] M. Muskat and F. Morgan, J. App. Phys. 9, 393 (1938).

[2] B. Tower, Proc. Inst. Mech. Eng. (a) 632–59 (1883); (b) 29–35 (1884).

lubrication as developed by Osborne Reynolds.[3] The occurrence of a friction minimum at the transition point between "partial lubrication" and "complete lubrication" was demonstrated by R. Stribeck,[4] who obtained curves showing the variation of the coefficient of friction with relative surface velocity for different values of the load. Sommerfeld[5] plotted the frictional torque as predicted from his theory for the infinitely long bearing against the journal velocity for several values of the load, and explained how all of the curves could be made to coincide by properly stretching or shrinking the scale of ordinates and abscissas to correspond to the load used. Hersey[6] apparently was the first to plot f against the dimensionless variable $\mu N/P$, where μ is the viscosity, N the speed of rotation, P the load per unit of projected bearing area, and f is the coefficient of friction, obtained by dividing the frictional force by the bearing load. Data for this plot were obtained by varying independently μ, N, and P, and although a general trend may be noted in the experimentally determined points, much is left to be desired in consistency.

In addition to a spread at low values of $\mu N/P$ which is customarily explained on the basis of "oiliness," most published curves have two common characteristics, namely, a friction minimum and a positive intercept on the friction axis of the straight line portion of the experimental curve obtained for the higher values of $\mu N/P$. While a minimum of friction is predicted by the Sommerfeld theory, curve I, Fig. 1, the observed friction coefficient, curve III, Fig. 1, rises to many times the theoretically predicted value at very low values of $\mu N/P$. Moreover, the observed transition point has been found at different values of $\mu N/P$ by different observers as well as for various bearing materials. McKee and McKee[7] and Dickinson and Bridgeman[8] have attributed the friction axis intercept to the effects of side leakage and lack of concentricity of the journal and bearing. In the absence of any theory for the bearing of finite length this explanation was obviously as good as any other, although on this basis the intercept might be expected to decrease as the ratio of length to diameter increased, while it actually was observed to decrease to a minimum and then increase.

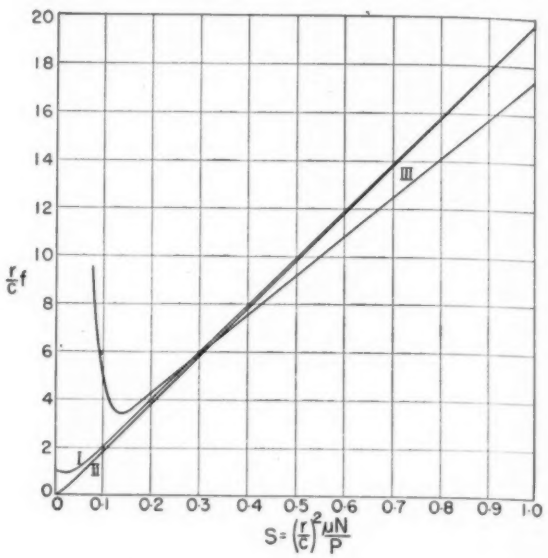

FIG. 1. Theoretical and experimental friction coefficient curves for full journal bearings. I, Sommerfeld curve for the friction on the journal of an infinitely long journal bearing; II, Harrison curve for the friction on the bearing of an infinitely long journal bearing; III, trend of typical published experimental data on full journal bearings. r=journal radius; c=radial clearance; μ=lubricant viscosity; N=journal speed; P=bearing load per unit projected bearing area; f=friction coefficient.

Another group of investigators, including Gümbel[9] and Nücker,[10] have given most of their attention to experiments designed to give information on the pressure distribution in the film, journal eccentricity, and lubricant flow, believing that friction data have little significance because of variations in temperature and viscosity around the journal.

The lack of a comprehensive theory has also been evident in the case of the film pressure distributions. Many writers apparently have

[3] O. Reynolds, Phil. Trans. Roy. Soc. **177**, 157 (1886).
[4] R. Stribeck, Zeits. V. D. I. **46**, 1340 (1902).
[5] A. Sommerfeld, Zeits. f. Math. Phys. **50**, 97 (1904).
[6] M. D. Hersey, *Theory of Lubrication* (1936), p. 89.
[7] S. A. McKee and T. R. McKee, Mech. Eng. **51**, 593–95 (1929).
[8] H. C. Dickinson and O. C. Bridgeman, J. S. A. E. **31**, 278 (1932).
[9] L. Gümbel, Jahrb. Schiffbautech. Ges. **18**, 236 (1917).
[10] W. Nücker, V. D. I., Forschungsheft 352 (1932).

assumed that the total lubricant source pressure should simply be added to the pressure due to the viscous drag at each and every point even though flow occurs, and the pressure must, in general, be equal to that of the atmosphere at the end of the bearing. The popular belief that the lubricant source, to be effective, must be placed in the region of low or negative pressure seems to have originated in this way.

Although a great deal of information can undoubtedly be obtained from a systematic study of the pressure distribution, journal eccentricity, and the effect of the position and strength of the source upon the load carrying capacity and friction, this paper will be confined entirely to friction studies in the thick film region for a fixed position of the source.

Experimental Arrangement

Journal bearing testing machines may be divided into two general classes. In one group the torque is measured on the bearing which must be capable of a slight rotation, while in the other the torque on the journal, i.e., on the rotating shaft, is measured. Examples of the first class are the machines of Barnard, Myers and Forrest,[11] McKee and McKee,[12] Stanton,[13] Jakeman,[14] Nücker,[10] and the Kingsbury machine[15] at Pennsylvania State College. The second class is illustrated by the apparatus of Pigott and Lane[16] of this laboratory and of Neely.[17] The chief advantage of the second class is that the bearing is fixed and auxiliary measuring apparatus may be easily applied. However, this advantage has so far only been acquired at the expense of simplicity or by the addition of supporting members which may have an effect upon the torque. Consequently the machine described here has been designed to measure the torque on the bearing.

Naturally the most important link in any apparatus for the study of journal bearing lubrication is the journal bearing itself. Since the theory for the bearing of infinite length was to be used for the determination of r/c, the ratio of journal radius to radial clearance, an approach to this state by making the bearing long in comparison to its diameter was desirable. However, in order to facilitate the eventual mounting of measuring instruments in the bearing surface as well as to minimize distortion an appreciable diameter was necessary. As a compromise a bearing surface $3\frac{1}{2}$ inches in diameter by $9\frac{3}{4}$ inches long was chosen. Since, in most practical cases, the ratio of journal diameter to diametral clearance is of the order of 1000, this figure was originally chosen as suitable. But when the surfaces were completed the ratio was approximately 1400. The journal, which was hardened, ground and lapped, was constructed of steel. The bearing consisted of a bronze bushing pressed into a steel jacket. The journal, which was supported by two self-aligning roller bearings, was driven through a flexible coupling by a Graham variable speed transmission (cf. Fig. 2). Speeds from 0 to 680

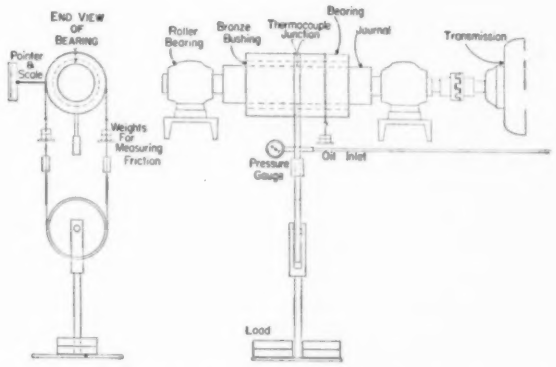

Fig. 2. Schematic diagram of journal bearing system.

r.p.m. were available, although the maximum for these experiments was about 400.

In order to reduce the effect of extraneous torque the bearing was left as nearly free to float on the journal as possible. A piece of $\frac{1}{8}''$ steel tubing about 30″ long, one end of which was rigidly fastened to the frame but electrically insulated from it, was run parallel to the axis of

[11] D. P. Barnard, H. M. Myers and H. O. Forrest, Ind. and Eng. Chem. **16**, 347 (1924).
[12] S. A. McKee and T. R. McKee, Trans. A. S. M. E. **59**, 721 (1937). See also O. C. Bridgeman, Physics **5**, 125 (1934).
[13] T. E. Stanton, *Friction* (1923).
[14] C. Jakeman, Engineering **109**, 866 (1920).
[15] E. M. Barber and C. C. Davenport, Bulletin No. 42, Pennsylvania State College.
[16] R. J. S. Pigott and A. A. Lane, U. S. Patent No. 2,033,588.
[17] G. L. Neely, Proc. Am. Petroleum Inst. **13**, 60–73 (1932).

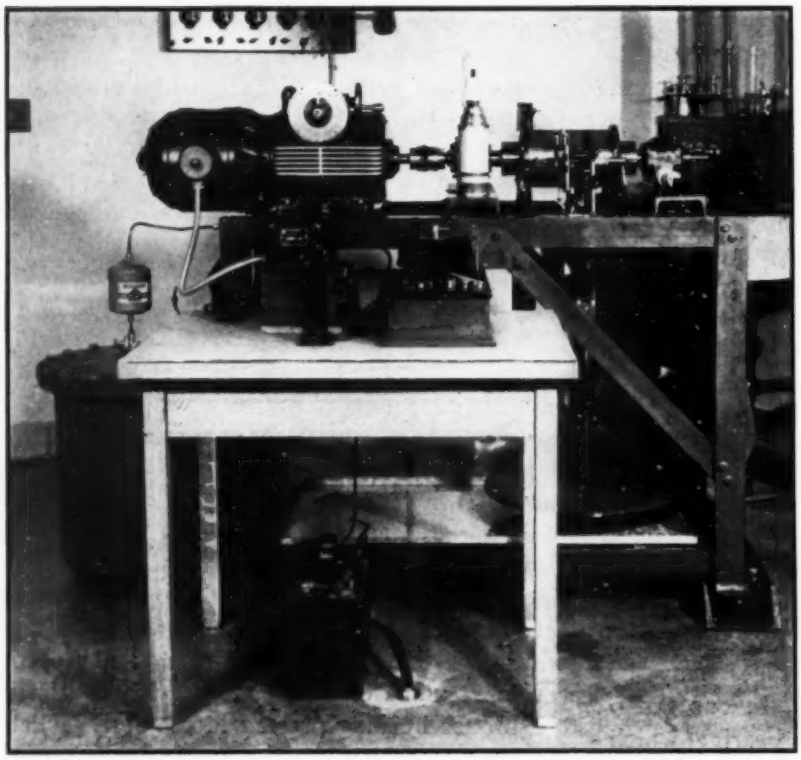

FIG. 3. Photograph of journal bearing system.

the bearing and served both to fix the bearing endwise and to conduct lubricant into the bearing. This, of course, introduced a restoring force, proportional to the displacement, when the bearing left its equilibrium position. But since the bearing was always brought back to its zero position, as determined by a micrometer eyepiece and pointer, for a torque determination, the elastic effect of the tubing was definitely advantageous in rendering the equilibrium position more stable. The friction torque was counterbalanced by weights on cords wrapped about the bearing, the load being supported in the same manner by steel tapes. The average of readings for both directions of rotation was considered to give the true torque. A torque due to the weight of one gram could be detected, although variations in torque at times made the readings less accurate. Since light loads were used in order to minimize bending and distortion of the journal and bearing, it became necessary to make N small so that $\mu N/P$ might be reduced to the desired lower limit. While this procedure made the measurement of relatively small values of torque imperative, it possessed the advantage that very little heat was generated. Consequently for values of $\mu N/P$ up to the limit of Fig. 1 the temperature of the bearing and of the lubricating film did not differ noticeably from room temperature. At low rates of shear, the implicit assumption that the viscosity of the liquids used is independent of the rate of shear also seems to be less questionable.

Since the viscosity of most liquids decreases quite rapidly as the temperature is increased, slight variations in temperature may influence the torque to a considerable extent. Thus some method of determining the true or average film viscosity is necessary. This problem is rendered difficult both because the film is extremely thin (of the order of a few thousandths of an inch) and the temperature may be expected to vary around the bearing. Thermometers and thermocouples have been used for measuring bearing and film temperatures, many workers attempting to maintain a constant and uniform temperature by the use of running water. Nevertheless, at high rates of shear considerable heat must be generated and surprisingly large variations in temperature may pass unnoticed. Film temperature determinations in these experiments have all been made with a single copper-constantan thermocouple located at the top of the bearing (load downward), 180° from the oil inlet, and in direct contact with the film. Temperatures were recorded to 0.1°C. The viscosities of the two oils used were determined with a Saybolt viscometer, that of the 2-ethylbutyl alcohol with an Ostwald pipette. All readings were converted to centipoises. The time of flow in every case was well in excess of the minimum allowable, the error being probably less than 1 percent.

Lubricant was forced into the bearing by air pressure, the maximum available being about 100 lb./in.^{2}.

Figure 3 is a photograph of the machine as it was arranged for these experiments. Some changes have since been made, the most important of which has been the mounting of the motor and transmission on a separate frame in order to minimize the effects of vibration.

Experimental Results

The upper line in Fig. 4 represents the curve

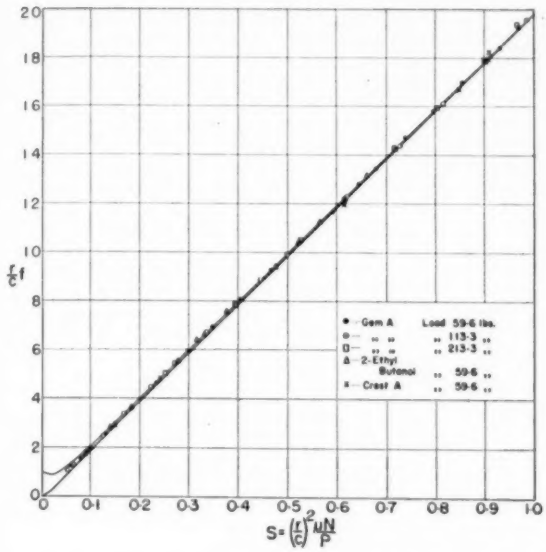

Fig. 4. Theoretical and experimental friction coefficient curves. I and II, Sommerfeld and Harrison curves as in Fig. 1. The points correspond to experimental data plotted on the assumption that $r/c=1470$.

predicted by the Sommerfeld theory for a bearing of infinite length when the torque on the journal is measured, while the lower line corresponds to the expected torque on the bearing. The Petroff theory for a journal running concentric with the bearing predicts a line through the origin of slope $2\pi^2$, which would lie between the two curves shown, and be approached asymptotically by both. Since the deviation of either curve from the common asymptote at the higher values of $(\mu N/P)(r/c)^2$ is small, it seems safe to assume that, for a relatively long finite bearing, the difference between the observed curve and its asymptote, which has been shown to be the Petroff line, will be negligible at the maximum value of the abscissae. Consequently the Petroff formula should be accurate enough for determining the ratio of r/c. Thus when the values $f=1.22\times10^{-2}$, $\mu N=7.26\times10^{-7}$ lb./in.^{2}, and $P=1.74$ lb./in.^{2}, which correspond to the highest value of $(\mu N/P)(r/c)^2$ used for 2-ethylbutyl alcohol, are substituted in the Petroff equation:

$$f=2\pi^2(r/c)(\mu N/P),$$

r/c is found to be 1470. This value of r/c was used in the plot of the data shown in Fig. 4, the points all being obtained for inlet pressures of about 10 lb./in.^{2}. Two oils, Gulf Gem A and Gulf Crest A, and 2-ethylbutyl alcohol of viscosity 13.3, 51.1, and 3.22 C.P. respectively at 25°C, as well as three values of the load for Gulf Gem A, were used. Due largely to variations in room temperature the actual film temperature varied between 23 and 33°C.

The points plotted in Fig. 4 were obtained at low journal speeds when the rate of shear was relatively low. As long as this condition was maintained the measured film temperature did not differ appreciably from the temperature of the room because little heat was generated. The situation is radically different, however, when the journal is running much faster and the

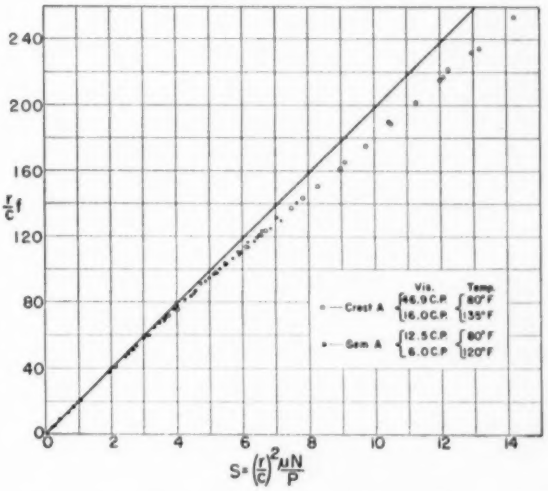

Fig. 5. Friction data showing the deviation of experimental results from the line corresponding to $r/c=1470$ at high values of S.

film temperature accordingly much higher. Fig. 5 shows the data obtained for Gulf Gem A and Gulf Crest A for values of $(r/c)^2(\mu N/P)$ up

to 14. The straight line is again the asymptotic limit for $r/c=1470$. Here the temperature indicated by the thermojunction was as much as 60°F above the room temperature and the bearing shell temperature, as indicated by a thermometer, was only slightly below the indicated film temperature. The points were obtained by driving the journal at the maximum speed until some degree of equilibrium had been attained, after which readings were taken as N was decreased.

As stated before, the experimental data for Fig. 4 were obtained for an inlet pressure of about 10 lb./in.^{2}. In Fig. 6 the lower line repre-

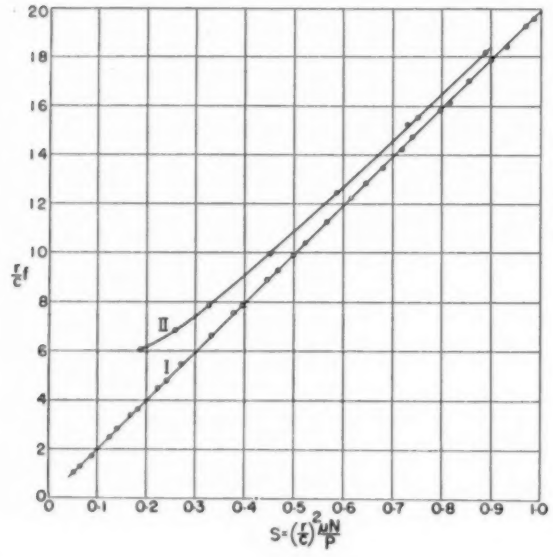

FIG. 6. Friction curves illustrating the effect on friction of source pressure. I, Pressure about 10 lb/in.^{2}. II, Pressure about 85 lb./in.^{2}.

sents these readings while the points on the upper line were secured when the pressure was about 85 lb./in.^{2}. The load used in this case was 59.6 lb.; the oil was Gulf Gem A. At high pressures the uncertainty of a torque determination is perhaps somewhat greater than at low pressures since vibration of the pointer is more pronounced. As in the other cases, the oil inlet was at the lowest point of the bearing.

The pressure effect was found to be reversible, that is, curves of torque *vs.* pressure were identical for pressure increasing or pressure decreasing.

DISCUSSION

Perhaps the most significant result of the above experiments is the fact that the experimental points in Fig. 4 fall, within the limits of experimental error, on a straight line which, when extended, passes through the origin. These data must not be interpreted as indicating that no "thin film" region was observed, because readings were discontinued when uncertainties in torque readings began to appear. This lower limit, in most cases, was observed to correspond to the point at which the electrical resistance of the oil film dropped from extremely high values to practically zero, indicating that some contact between journal and bearing had taken place. Further work in this transition region is necessary before definite conclusions can be drawn.

The determination of a precise value of the clearance, upon which the slope of the experimentally determined line in Fig. 4 depends, was regarded by Reynolds[3] as impossible. Unfortunately the situation does not seem to be much better even now. For even though the radii of the journal and bearing should be known to ± 0.0001 inch, which has been the limit of measurement in this case, an error of as much as 15 percent in r/c would still be possible. Accordingly, the method suggested and adopted by Reynolds[3] of determining the clearance from measured values of the friction and viscosity has been used.

The fact that the value of r/c determined in this way agrees very well with that obtained from capacity measurements for relatively high journal speeds seems significant, although it is not evident that the same average value should be expected in both cases. The resistance of the oil dielectric was very high so that the capacity bridge balance was readily obtained. The measured capacitance was 43,800 $\mu\mu f$, which corresponds to a radial clearance of 1.18×10^{-3} inch or to an r/c of 1460. The agreement between this value and that obtained from the Petroff formula is thus extremely good. The measured value* of the dielectric constant used in this calculation was 2.18.

* We are indebted to Dr. W. N. Arnquist of this laboratory for this determination.

Obviously the tendency of the observed points to lie on a straight line which, when extended, passes through the origin will in no way be affected by changes in the value of the clearance. The clearance determines only the slope of the line.

The explanation of the tendency observed in Fig. 5 for the experimental data to turn away from the straight line (corresponding to $r/c = 1470$) through the origin at high values of $\mu N/P$ is not entirely certain. In fact, on first thought it might be concluded that at higher values of $\mu N/P$ the data determine a straight line which does not pass through the origin but has a positive intercept on the friction axis. This, however, is unlikely. Rather the apparent discrepancy is probably due to the method of taking data and of determining the value of the viscosity. That is, the deviation of the points from the straight line results from the failure to determine the correct average temperature of the film when this temperature rises much above that of the room. This explanation is in agreement with experiment insofar as the deviation would be in the same direction but much greater were no correction whatever made for the effect of temperature on viscosity.

Even in experiments in which the journal and bearing are water cooled, the film temperature cannot, with certainty, be regarded as uniform at all points. In addition to the normal heat conductivity, skin effects might have an appreciable influence upon the rate of dissipation of heat. This view again corresponds to the conclusions of others. For example, even though Tower flooded his bearing with oil and maintained a journal temperature of 90°F, Reynolds[3] estimated that the film temperature was increased by as much as 15° due to friction.

The deviation of the data for high values of $\mu N/P$ from the straight line determined by the data for low $\mu N/P$ might also be accounted for on the basis of a decrease in viscosity at higher rates of shear. This explanation does not seem probable, however, in view of the evidence, not always convincing to be sure, against it. Thus Hatschek[18] reports that Duff found no observable difference in the viscosity of a "heavy kerosene" for velocity gradients up to 20,000 cm/sec./cm. Similarly Kingsbury,[19] Bulkley,[20] and Arveson[21] report that for lubricating oils investigated, no deviations from the ordinary laws of viscous flow were observed up to rates of shear of approximately $26 \cdot 10^4$, $5 \cdot 10^3$ and 10^5 sec.$^{-1}$, respectively. On the other hand Neale[22] has interpreted some of his results, for rates of shear less than $6 \cdot 10^4$, as indicating a decrease in viscosity at the higher rates of shear. The maximum rate in these experiments, which was reached in securing the data for Fig. 5, was about $5 \cdot 10^4$ sec.$^{-1}$.

Some method of determining the actual film temperature at different points about the bearing is highly desirable. In the absence of such information, data in which the heat generated is insufficient to raise the temperature by a measurable amount seem the most convincing.

The fact that the friction coefficients at 85 lb. inlet pressures are higher than those for 10 lb. inlet pressure (cf. Fig. 6) confirms qualitatively the theory developed in part I. The increase of the friction coefficient is larger than was originally expected, but quantitative comparisons cannot be made because the theory was developed for the case in which the source is always at right angles to the line of centers. This condition was undoubtedly not met in these experiments because the source was always maintained at the bottom of the bearing. The effect of the bearing depressing force, which is the manifestation of the force that tends to separate the surfaces near the oil inlet, is particularly noticeable at the high pressures employed. Thus while data for $\left(\frac{r}{c}\right)^2 \frac{\mu N}{P} = 0.05$ were secured without difficulty at the low pressures of Fig. 4, irregular effects and a tendency toward seizure became apparent at values as high as 0.18 at the higher pressure.

Since the friction has been observed to increase as the source pressure is increased, a curve lying below the line in Fig. 4 might be expected for pressures below 10 lb./in.^{2}. However, since the rate of change of the friction with

[18] E. Hatschek, *The Viscosity of Liquids* (1928), p. 60.

[19] A. Kingsbury, Mech. Eng. **41**, 537 (1919).
[20] R. Bulkley, Nat. Bur. Stand. J. Research **6**, 89 (1931).
[21] M. H. Arveson, Ind. and Eng. Chem. **24**, 71 (1932).
[22] S. M. Neale, Chemistry and Industry, Feb. 6 (1937).

pressure has been found to be much less at low than at high pressures, the effect upon the friction of a further reduction in pressure will be entirely negligible.

This increase of torque cannot be due, to any appreciable extent, to a change of viscosity with pressure. Using the recent data of Dow,[23] it is found that the maximum contribution to the friction due to a uniform increase in pressure equal to that applied at the lubricant source could not be greater than about two percent. Furthermore, the actual contribution should be much less than the maximum value because the negative pressure gradient near the source is quite large, and the residual pressure increase at points distant from the source is very small.

The study of the effects of the amount of flow upon the torque is being continued with a modification of the apparatus which permits of rotation of the bearing so that the fluid may also be introduced at 90, 180, and 270 degrees from the lowest point. Additional apparatus, designed with the intention of either permitting or eliminating wedging of the film, is being constructed for a study of the thin film region. Meanwhile an analysis, by the method of successive approximations, of the case in which the source remains fixed at any angle with respect to the load line is being made. The results of these studies will be reported in later papers of this series.

The authors are indebted to Mr. D. W. Reed for assistance with the experiments, and to Dr. Paul D. Foote, executive vice president of the Gulf Research & Development Company, for permission to publish the paper.

[23] R. B. Dow, J. App. Phys. **8**, 367 (1937).

X-Ray Investigation of the Form of Acetylsalicylic Acid in Certain Sugars

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X-ray studies of samples made of sucrose, glucose, and acetylsalicylic acid were made to determine if the latter is in solid solution with the sugars. The main constituent of the samples was sucrose and the amounts of acetylsalicylic acid varied from one and a half to twenty per cent. The samples were prepared by melting and heating the sugar combinations to 160°C, removing essentially all the water and allowing to cool. The acetylsalicylic acid was then incorporated in one set of samples at 140°C and in another at a temperature between 110–115°C, that is, both above and below the melting point (133–5°C) of the compound. The former samples were far more hygroscopic than the latter, but in neither case did the acetylsalicylic acid seem to form a solid solution with the rest of the constituents.

I. Introduction

IT has been recently claimed[1] that when acetylsalicylic is incorporated in a sugar combination of sucrose and glucose, while the sugars are molten but at a temperature below the melting point of acetylsalicylic acid (133–5°), the combination results in the formation of a solid solution. Whether such a combination forms a solid solution when the acetylsalicylic acid is incorporated at a temperature above its melting point, is also not definitely known. These problems were approached from the x-ray standpoint, and the results of the x-ray study are described in this paper.

The samples studied here were prepared by melting and heating the sugar combination of seventy percent sucrose and thirty percent glucose to 160°C, removing essentially all the water and allowing to cool. The acetylsalicylic acid was then incorporated in one set of samples at 140°C and in another at a temperature between 110–115°C, and varied in amounts from one and a half to twenty percent. A few samples were pre-

[1] E. C. Merrill, Chem. Abs. **31**, 5949 (1937).

pared by adding two to three percent fructose to the above constituents. The sucrose, glucose, acetylsalicylic acid and fructose used in preparing these samples were of U.S. pharmacopoeia and Eastman grade.

II. Experimental Procedure

The x-ray powder photograms were made by the usual Debye-Scherrer-Hull method. Portions of the materials, ground to a fine powder, were mixed with a small amount of collodion; the mixture was then packed into a 19-gauge stainless steel hypodermic needle tubing with internal diameter of 0.7 millimeter, compressed with a plunger, and finally extruded as a compact cylinder of the same diameter. The steel tubing was then mounted in a cylindrical x-ray camera of 57.3 millimeters effective diameter in such a way that only the extruded part of the specimen appeared in the x-ray beam. The specimens were rotated during the exposure. The use of the standard size specimens leads to data which are strictly comparable in themselves, regardless of errors in the apparatus or in the measurements of the dimensions of camera.

The photograms were made with filtered copper $K\alpha$ radiation of effective wave-length 1.5374A, which was supplied by a Phillip's type demountable x-ray tube equipped with an aluminum window of 0.0005 inch thickness. The current through the tube was 20 milliamperes and the impressed voltage 45 kilovolts peak.

The specimens of the sugar combinations in which the acetylsalicylic acid was incorporated above its melting point were very hygroscopic. They were mounted and preserved in a special loading box made for substances which take up water in air and were transferred to the closed x-ray camera just before exposure. With non-screen x-ray films an exposure time of 15 minutes was found to be sufficient for satisfactory photograms.

The interplanar spacings calculated from the diffraction angles measured on the photograms have been plotted on semi-logarithmic coordinate paper. Identification of pure substances can be made readily by viewing the chart of the data obtained by superimposing on reference charts for the substances sought.

III. Results

(A) Sucrose

The observed interplanar spacings and intensities of diffraction lines obtained from the sample of sucrose are given in Table I. For comparison

Table I. *Interplanar spacings for sucrose.*

Observed Spacing	Estimated Relative Intensities	Calculated Spacings and Indices	
A			
6.64	V.S.	6.65	(101)
5.56	S.	5.54	(111)
4.43	V.S.	4.42	(210)
3.55	V.S.	3.55	(030)
3.26	M.	3.24	(221) (311)
2.74	S.	2.73	(321), 2.72 (031) (222)
2.47	M.	2.46	(410)
2.31	S.	2.32	(032)
2.22	M.	2.22	(330)
2.08	M.	2.08	(141)
1.90	S.	1.90	(004) (033), 1.92 (341) (430)
1.79	M.	1.79	(404)
1.70	M.	1.71	(600) (151)
1.58	W.	1.59	(105)
1.52	W.	1.52	(070)
1.46	M.	1.46	(044) (700), 1.47 (361)
1.41	W.	1.40	(505) (161) (260)
1.34	W.	1.33	(080) (550)
1.31	W.	1.32	(106)
1.27	M.	1.28	(800)
1.21	W.	1.22	(171), 1.19 (606)
1.17	W.	1.17	(036)
1.12	S.	1.12	(280) (107)
1.08	W.	1.08	(181), 1.07 (480)
1.05	W.	1.05	(182)
0.97	W.	0.97	(008) (066) (290)

V = Very; S = Strong; M = Medium; W = Weak.

the corresponding interplanar spacings have been computed from the previously published data[2] on the crystal structure of this substance and the Miller indices of the corresponding planes have been assigned. The relation between the Miller indices, hkl, the lattice parameters a_0, b_0, c_0, and β and the interplanar spacings, d, which were used for this computation, is:

$$d=\frac{b_0\times\sin\beta}{\left(\frac{h^2}{a^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}+k^2\sin^2\beta\right)^{\frac{1}{2}}} \qquad (1)$$

where $a=a_0/b_0$, $c=c_0/b_0$, $a_0=10.65$A, $b_0=8.70$A, and $\beta=105°\ 44'$.

Diffraction lines which gave interplanar spac-

[2] K. Becker, and H. Rose, "X-Ray Spectroscopy of Organic Compounds," Zeits. f. Physik **14**, 369 (1923).

ings less than one angstrom were not included in the Table I, since their value in the identification of the compound was relatively small.

(B) Glucose

The observed interplanar spacings and intensities obtained from the photogram of the sample of glucose together with the theoretical values of interplanar spacings and the indices of the diffraction planes are given in Table II.

TABLE II. *Interplanar spacings for glucose.*

Observed Spacings	Estimated Relative Intensities	Calculated Spacings and Indices
A		*A*
6.88	M.	6.88 (101)
6.01	W.	6.00 (10$\bar{1}$)
4.47	V.S.	4.46 (102), 4.45 (011)
3.87	S.	3.86 ($\bar{1}$11) (11$\bar{1}$)
3.47	W.	3.46 (012)
3.11	S.	3.11 (103)
2.90	W.	2.88 (300)
2.72	W.	2.74 (203)
2.54	M.	2.52 (020)
2.43	M.	2.42 (120)
2.18	M.	2.18 (122) (220)
2.03	W.	2.03 (222)
1.86	W.	1.86 (223)
1.74	V.W.	1.73 (500), 1.72 (404) (024)
1.69	V.W.	1.68 (030), 1.67 (224)
1.61	V.W.	1.60 (422)
1.41	V.W.	1.42 (424)
1.34	V.W.	1.35 (333)
1.30	V.W.	1.31 (425)
1.23	V.W.	1.23 (700)
1.19	V.W.	1.19 (008) (242)
1.16	V.W.	1.15 (340)
1.10	V.W.	1.11 (044), 1.09 (440)
1.08	V.W.	1.08 (800)

While anhydrous alpha-*d*-glucose crystallizes in in orthorhombic structures[3] and is the one often referred to in the literature on sugars, alpha-*d*-glucose monohydrate is monoclinic.[4] The sample used for the present investigation was also monohydrate glucose. The theoretical values were computed by means of Eq. (1) where $a_0=8.72$A, $b_0=5.03$A, $c_0=9.59$A, and $\beta=97°\ 59'$.

(C) Acetlysalicylic acid

The observed interplanar spacings and intensities obtained from the photogram of the sample of acetylsalicylic acid together with theoretical values of interplanar spacings and the indices of the diffraction planes are given in Table III. Some conflicting data[5] on this compound are found in literature; the interplanar spacings given in this table, however, have been computed from consistent values of the lattice parameters determined by Niini,[6] and Nitta and Watanabe.[7] The theoretical interplanar spacings were computed by means of Eq. (1), using $a_0=11.37$A, $b_0=6.54$A, $c_0=11.37$A, and $\beta=95°\ 42'$.

TABLE III. *Interplanar spacings for acetylsalicylic acid.*

Observed Spacings	Estimated Relative Intensities	Calculated Spacings and Indices
A		*A*
5.66	V.S.	5.66 (200), 5.68 (110)
4.32	M.	4.30 (210)
3.92	V.S.	3.92 (11$\bar{2}$)
3.30	V.S.	3.30 (203)
3.06	V.W.	3.06 (121)
2.77	W.	2.79 (122)
2.50	W.	2.48 (320)
2.18	W.	2.18 (205) (030)
2.11	V.W.	2.12 (131), 2.09 (404)
2.00	V.W.	2.02 (132)
1.90	W.	1.89 (106)
1.83	V.W.	1.84 (220)
1.78	V.W.	1.76 (306)
1.44	V.W.	1.43 (630)
1.40	V.W.	1.41 (208), 1.39 (118)
1.34	V.W.	1.32 (408)
1.25	V.W.	1.26 (901)
1.21	V.W.	1.22 (640)

(D) Fructose

The observed interplanar spacings and intensities of diffraction from fructose together with the theoretical values of interplanar spacings and the indices of the diffracting planes are given in Table IV. As this sugar crystallizes in simple orthorhombic structure[3] the theoretical interplanar spacings were calculated by means of the relation:

$$d=\frac{b_0}{\left(\frac{h^2}{a^2}+K^2+\frac{l^2}{c^2}\right)^{\frac{1}{2}}}, \qquad (2)$$

[3] J. Hengstenberg and H. Mark, "The Lattice Structure of Some Simple Sugars," Zeits. f. Krist. **72**, 301 (1929–30).
[4] O. L. Sponsler and W. H. Dore, "The Crystal Structure of Some Forms of Glucose," J. Am. Chem. Soc. **53**, 1639 (1931).
[5] R. Kozu and K. Takane, Proc. Imp. Acad. Tokyo, **381** (1935).
[6] R. Niini, Zeits. f. Krist. **79**, 532 (1931).
[7] I. Nitta and T. Watanabe, Sci. Papers Inst. Phys. Chem. Research, Tokyo **31**, 125 (1937).

TABLE IV. *Interplanar spacings for fructose.*

OBSERVED SPACINGS	ESTIMATED RELATIVE INTENSITIES	CALCULATED SPACINGS AND INDICES
A		*A*
6.05	S.	6.04 (101)
5.17	V.S.	5.18 (111)
4.23	V.S.	4.25 (120)
3.44	W.	3.43 (211) (102)
3.11	S.	3.10 (130) (122)
2.84	S.	2.86 (032)
2.48	S.	2.49 (311) (231)
2.23	S.	2.25 (312)
2.06	W.	2.07 (241)
1.88	M.	1.90 (151)
1.82	M.	1.83 (340) (421) (402)
1.73	W.	1.73 (430)
1.68	W.	1.68 (060)
1.58	V.W.	1.57 (440) (501)
1.52	V.W.	1.52 (261) (521)
1.45	W.	1.44 (531)
1.35	W.	1.33 (271) (600)
1.29	W.	1.29 (460) (620)
1.25	V.W.	1.25 (630) (371) (181)
1.21	M.	1.20 (280)
1.16	V.W.	1.16 (560) (470)
1.12	W.	1.12 (650) (711)
1.09	V.W.	1.10 (191)
1.05	V.W.	1.06 (480)
1.01	V.W.	1.00 (811)
0.98	V.W.	0.98 (490)

where $a = a_0/b_0$, $c = c_0/b_0$, $a_0 = 8.06$A, $b_0 = 10.06$A, and $c_0 = 9.12$A.

(E) Sugar combinations

The interplanar spacings calculated from the diffraction angles measured on the photogram of a combination of seventy percent sucrose and thirty percent glucose are shown graphically in Fig. 1, together with similar data obtained for

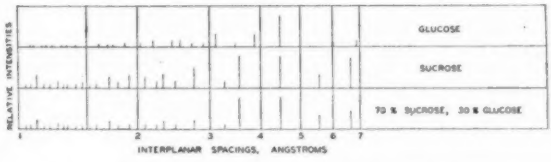

FIG. 1. Diffraction data for glucose and sucrose.

sucrose and glucose. The diffraction pattern of the combination indicates that it consists of the diffraction patterns of the two constituents superimposed and it is predominately that of sucrose. The strongest line of the pattern of glucose has practically the same interplanar spacing (4.47A) as one of the strongest lines of the pattern of sucrose. These two lines superimpose in the pattern of the combination and give the strongest line of the pattern. Addition of two to three percent of fructose does not make an essential change in the general pattern of the combination.

(F) Sugar combinations with acetylsalicylic acid

The diffraction patterns of the sugar combinations in which the acetylsalicylic acid was incorporated at a temperature below its melting point were as clear as the patterns of the constituents and contained sharp lines. It was possible to identify the acetylsalicylic acid as may be seen from Fig. 2. The diffraction pattern

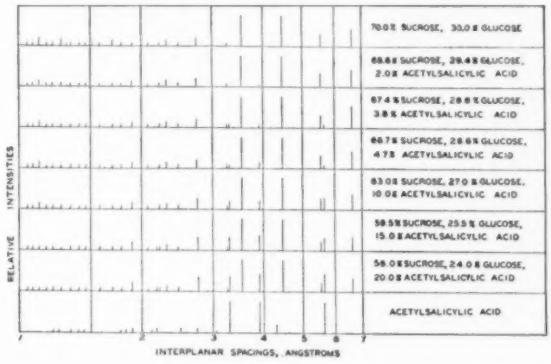
70.0 % SUCROSE, 30.0 % GLUCOSE
68.6 % SUCROSE, 29.4 % GLUCOSE, 2.0 % ACETYLSALICYLIC ACID
67.4 % SUCROSE, 28.8 % GLUCOSE, 3.8 % ACETYLSALICYLIC ACID
66.7 % SUCROSE, 28.6 % GLUCOSE, 4.7 % ACETYLSALICYLIC ACID
63.0 % SUCROSE, 27.0 % GLUCOSE, 10.0 % ACETYLSALICYLIC ACID
59.5 % SUCROSE, 25.5 % GLUCOSE, 15.0 % ACETYLSALICYLIC ACID
56.0 % SUCROSE, 24.0 % GLUCOSE, 20.0 % ACETYLSALICYLIC ACID
ACETYLSALICYLIC ACID
RELATIVE INTENSITIES
1
2
3
4
5
6
7
INTERPLANAR SPACINGS, ANGSTROMS

FIG. 2. Diffraction data for sugar combinations and acetylsalicylic acid.

of the acetylsalicylic acid contains three very strong lines, two of which overlap two lines of the diffraction pattern of the sugar combination without the acetylsalicylic acid and hence cannot be identified separately especially in the patterns of the combinations in which the acetylsalicylic acid is present in very small quantities. The third strongest line, however, appears very faintly in the patterns of samples of low acetylsalicylic acid contents. As the amount of the acetylsalicylic in sugar combinations is increased, not only the strongest lines of its pattern, but also the lines of the second strong subgroup become quite prominent. These lines match with those of the standard pattern of the acetylsalicylic acid. Both the positions and the intensity of these lines indicate clearly that the lines are superimposed on the diffraction pattern of the sugar combination and that no solid solution or complex compound formation has occurred.

The diffraction patterns of the sugar combina-

tions in which the acetylsalicylic was incorporated at a temperature above its melting point, although not very clear, contained enough sharp lines with sufficient intensity for identification. Except for excessive blackening they are identical with those of above samples, which indicates clearly that under the conditions these samples were prepared no solid solution has occurred.

IV. Discussion of Results

The results of this x-ray study may be summarized briefly as follows: In the case of the sugar combinations in which the acetylsalicylic acid was incorporated at a temperature below its melting point no solid solution or complex compound formation occurs. Those combinations in which the acetylsalicylic acid was incorporated at 140°C also show that under the condition these combinations were prepared, no solid solution has occurred. The latter preparations are, however, very hygroscopic. It seems that due to decomposition of the acetylsalicylic acid at 140°C the free acetic acid probably hydrolyzes the sucrose and thus renders the combination hygroscopic.

An attempt was made to determine the presence of the salicylic acid in the combinations due to the decomposition of acetylsalicylic acid, but no satisfactory match was found between the lines of the diffraction patterns of salicylic acid and the combinations. If the salicylic acid is present in these combinations, it may be in small quantities which cannot be detected by x-ray methods.

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